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Microwave-infrared double resonance of CH_4 using 3.39μ He–Ne laser line

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The rotational transition between the $F^{(2)}_1$ and $F^{(2)}_2$ components of the 6_7 $\nu_3 = 1$ level of CH_4 has been observed at 6895 MHz by double resonance experiments in the 3.39 μm He–Ne laser cavity. When the microwave radiation is applied the Lamb dip signal is observed to decrease markedly in size because of the double resonance coherence splitting phenomenon. A double resonance signal is also observed over the Doppler width of the CH_4 absorption because the population shift caused by the microwave transition reduces the saturation of the CH_4 absorption by the laser. The frequency of the transition was measured as 6895.3±0.3 MHz.

INTRODUCTION

Although CH_4 is a nonpolar molecule, it has a permanent dipole moment in a degenerate vibrational state as predicted by Mizushima and Venkateswarlu.[1] This dipole moment in the ν_3 state of CH_4 has been measured[2,3] from the Stark shift of doubly degenerate levels to be 0.02 D. In this paper we report an observation of a rotational transition of CH_4 in the ν_3 state caused by the small vibrational-induced dipole moment. The rotational transition at 6900 MHz occurs between two components of the 6_7 levels (total angular momentum 6 and rotational angular momentum 7) which are split by vibration–rotation interaction.[4] Because the Boltzmann factor for the ν_3 state is very small, the calculated absorption coefficient for this transition is of the order of 6×10^{-15} cm^{-1} and observation of this transition by conventional microwave absorption spectroscopy is impossible with currently available instruments. The power of double resonance for detecting such weak transitions has already been demonstrated.[5]

METHOD OF OBSERVATION

The portion of the energy level scheme of CH_4 of interest for this experiment is shown in Fig. 1 and Table I. The numbers in Table I were obtained by correcting the observed[6] splitting of the $P(7)$ line for the centrifugal distortion splitting of the ground state using the reported[6] value of t_{044} and the calculations of Dorney and Watson.[7] The symmetry numbering adopted here is the Hougen (subscript)—Jahn (superscript) system recommended by Hougen.[8]

The $F_1^{(2)} \leftarrow F_2^{(2)}$ component of the $P(7)$ rotational transition of the ν_3 fundamental coincides very closely with the maximum of the gain curve for the pressure shifted 3.39μ laser line.[9,2] Therefore, a double resonance experiment can be conducted using the 3.39μ He–Ne laser line as the signal radiation (ν_s) and microwave radiation at the frequency appropriate to the $F_2^{(2)}$ to $F_1^{(2)}$ energy difference (predicted 6890 MHz) as the pumping radiation (ν_p). There are two methods of detecting the double resonance effect: (a) observation of coherence splitting of the signal lines and (b) observation of intensity variation of the signal caused by the population change due to pumping. Both methods are used in this paper.

Coherence Splitting of the Lamb Dip

The Doppler width of the methane absorption is about 150 MHz. This is too large for the observation of the coherence splitting phenomena with achievable microwave electric fields which are limited by electric breakdown of the CH_4 to about 10^4 V/cm. However, the coherence splitting of the Lamb dip can be obtained.[10,11]

TABLE I. Energy levels of the 6_7 $v_3=1$ states of CH_4.

Symmetry	Energy[a] (GHz)
$F_2^{(2)}$	−6.89
E	−2.88
$F_1^{(2)}$	0
A_1	5.64
$F_1^{(1)}$	14.18
$F_2^{(1)}$	15.62

[a] These energy levels were calculated from the data of Ref. 6. The estimated uncertainty is 0.1 GHz. The energies are tabulated relative to the $F_1^{(2)}$ level.

The Lamb dip in CH_4 was first observed by Barger and Hall.[12] They found it possible to stabilize the frequency of the He–Ne laser to this Lamb dip. The frequency stability achieved (~1 kHz) is good enough to suggest that the wavelength of the stabilized 3.39μ laser be used as standard of length. Much of the motivation for carrying this work through comes from a suggestion by Hall[13] that the microwave double resonance might be used to modulate the Lamb dip and thus remove the possible slope of the laser gain curve as a source of error in the stabilized frequency.

By irradiating the methane sample with a high power microwave source at the $F_1^{(2)}$ to $F_2^{(2)}$ transition frequency the Lamb dip can be significantly broadened by the double resonance effect. In the apparatus used in the present experiment the Lamb dip is calculated to be about 300 kHz wide in the low pressure region. In the double resonance experiment it is split by $\mu_{12}E/h$. If the microwave electric field can be made large enough to make these splittings a few megahertz, the Lamb dip will be smeared out. Using the vibration induced dipole moment of 0.02 D it can be calculated that a microwave electric field of about 500 V/cm is required to split the transition by few megahertz. This field can be most easily achieved by using a resonant cavity. Further, the electric field of the microwave radiation should be perpendicular to the electric field of the laser radiation because the dipole matrix elements of high M_J are largest for a Q branch and the intense components of a P transition are of high M_J for perpendicular (but not parallel) selection rules.

Double Resonance over Doppler Profile

The detection of a population effect in this system would be difficult with a weak infrared source (and therefore the molecules in thermal equilibrium) because few molecules are in the ν_3 state. However, under strong laser radiation the transition is saturated and many molecules (with a certain velocity component) are in the excited state. The resonance microwave radiation changes the degree of saturation by depleting molecules from saturated levels and, therefore, a populational effect is observed with increased absorption of laser light. Such a double resonance effect under saturation conditions has been observed and discussed by Shimizu.[14] (In addition to the excited state population pumping effect described above, there is the possibility that there will be a similar signal caused by a coherence splitting in the saturation regime when the laser and microwave radiation electric fields are crossed.) For this experiment the frequency of the laser can be allowed to drift anywhere within the Doppler absorption profile of the CH_4 line. Consequently the microwave frequency can be swept over the pump frequency without simultaneously trying to control the laser frequency.

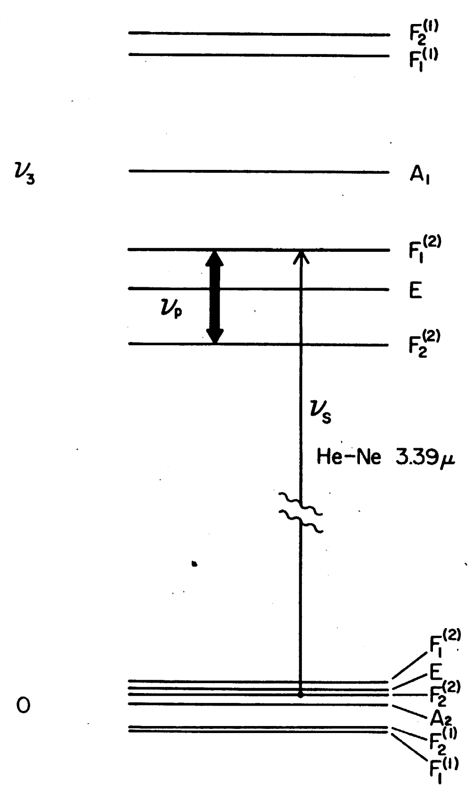

FIG. 1. The portion of the energy level scheme of CH_4 involved in the double resonance experiment. The spacings of multiplet in the ground state ($J=7$) are magnified for clarity. The transition observed in this work is indicated by the bold arrow ν_p and the laser transition is indicated by the arrow ν_s.

EXPERIMENTAL

The apparatus used in these experiments is diagrammed in Fig. 2. The microwave cavity used (at 6900 MHz) was constructed by shorting one end of a one wavelength long section of RG50/U rectangular waveguide ($1\frac{1}{2}\times\frac{2}{3}$-in. outer dimension) and placing a septum with a circular coupling iris at the other end. The Q of the cavity was about 1500. The laser radiation passes through quartz windows sealed over $\frac{3}{16}$-in. holes in the narrow face of the waveguide one quarter wavelength from the shorted end. The coupling of the cavity was adjusted with a slide screw tuner just before the iris as indicated in Fig. 2. With 5 W microwave power into the cavity at critical coupling the maximum microwave electric field was calculated to be slightly more than 1 kV/cm. The resonant frequency of the cavity could be tuned over about 120 MHz by inserting a quartz rod (3-mm diam) into the maximum electric field region. The search for the double resonance was made by setting the cavity resonance at particular frequency, adjusting the klystron reflector to the center of the cavity resonance, and looking for some effect on the Lamb dip. Then the cavity resonance was moved by 1 MHz and the process repeated.

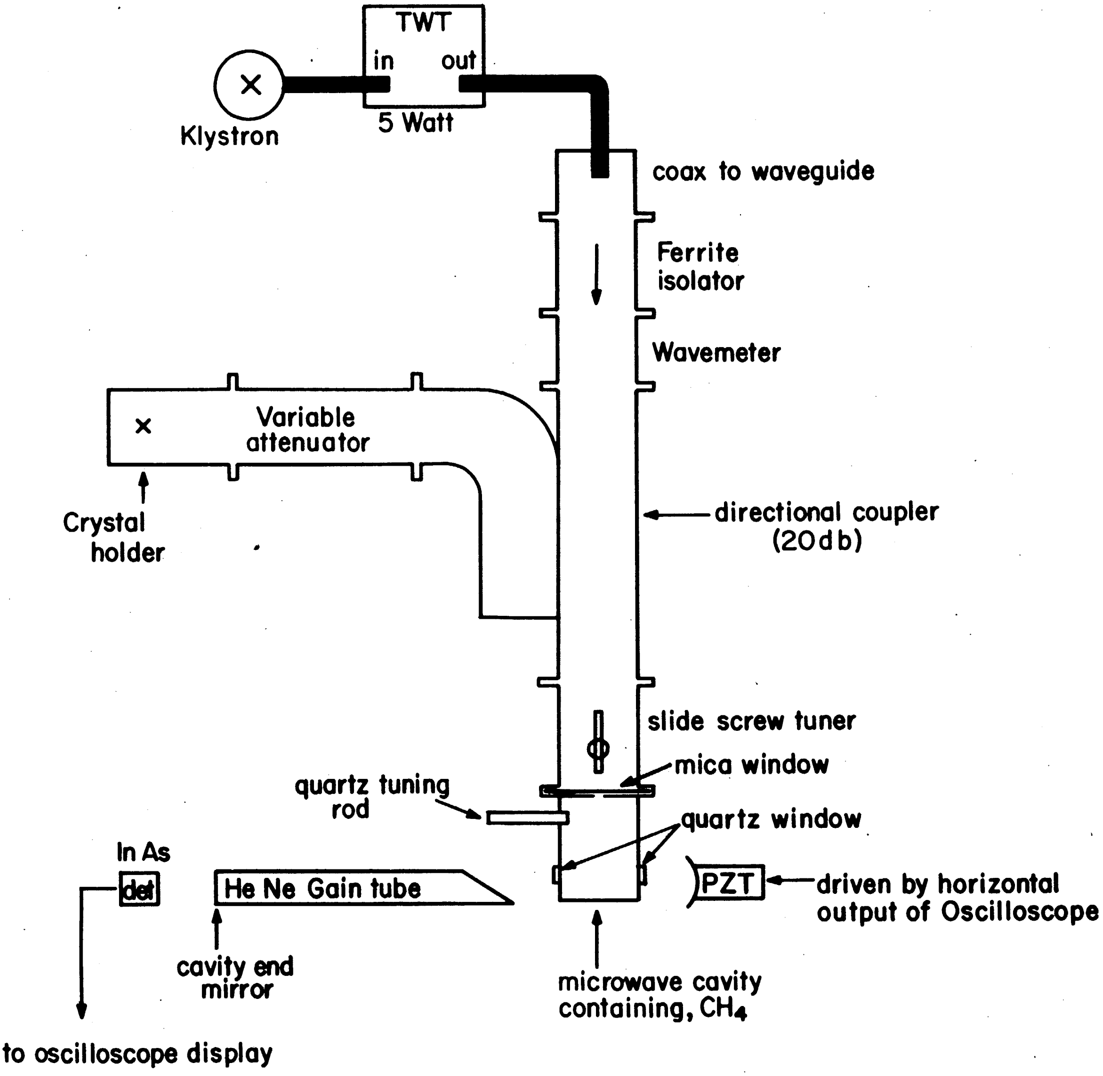

FIG. 2. The double resonance apparatus in the video detection arrangement. The laser cavity is 50 cm in length. The gain tube is about 38 cm long. The infrared detector is a Philco 1AU601. The TWT was a Litton L-5112. The klystron is a Sperry 2K44.

OBSERVATIONS

Coherence Splitting of the Lamb Dip

At 6895±1 MHz the Lamb dip is almost completely destroyed by the microwave radiation. The microwave radiation had no effect on the Lamb dip at other frequencies.

After the double resonance was observed with a cw microwave field, a modulation scheme was set up in which a 20-kHz square wave of 15 V amplitude was applied to the klystron reflector. During one half-cycle the klystron frequency coincided with the cavity resonance at 6895 MHz. During the other half cycle, the klystron was off its mode curve and not in oscillation. The output of the laser detector was amplified through a scope channel with a bandpass of 10 to 30 kHz and then sent to a phase sensitive detector at 20 kHz with a time constant of 1 msec. The Lamb dip could be seen quite clearly on the PSD output.

Double Resonance over Doppler Profile

In observing the signal after amplification but before the PSD, it was noted that there was a large 20 KHz component throughout the region of the laser gain curve near the Lamb dip. This signal disappeared on pumping out the CH_4 indicating that it results from a double resonance effect over the entire CH_4 Doppler profile. No similar signal was observed with the microwave cavity resonance at other frequencies.

In another experiment, a 20-kHz square wave of about 1 V amplitude was applied to the klystron reflector simultaneously with a sawtooth sweep at about 20 cycles. The output of the laser detector was amplified with a band pass of 10 to 30 kHz, introduced into a 20 kHz phase sensitive detector, and the PSD output displayed on the Y axis of an oscilloscope with the klystron sawtooth on the X axis. If the laser was tuned near the CH_4 absorption and the cavity resonance set near 6895 MHz, there was a strong derivative signal which is shown in Fig. 3. The transition frequency was measured by superimposing frequency markers on this signal. There should be some pulling of the center frequency of the double resonance signal by the cavity if the cavity resonance is not on the line center. However, this pulling appeared to be at most 0.4 MHz. The frequency for the $F_1^{(2)}$–$F_2^{(2)}$ transition obtained is 6895.3±0.3 MHz.

The existence of the double resonance component (population effect) not belonging to the Lamb dip poses some problems in using the double resonance to eliminate the gain profile background in laser stabilization. In the video Lamb dip experiment[12] the Lamb dip is about 1% of the total laser power. In the double resonance experiment the population effect and Lamb dip signals are comparable in magnitude. The dependence of the population effect signal on laser gain profile becomes very small as the extent of CH_4 saturation becomes very large.

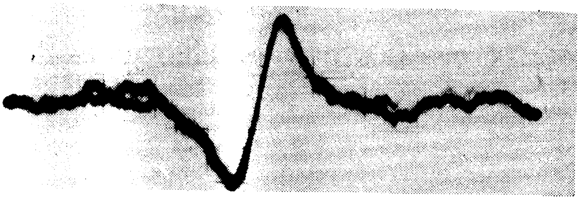

FIG. 3. The double resonance signal with swept microwave frequency. The microwave cavity is tuned to 6895 MHz which conicides with the frequency of the displayed signal. The klystron reflector is modulated with a 20-kHz square wave of 1 V amplitude. The output of a 20-kHz PSD (1-msec time constant) is displayed on the Y axis while the X axis and the klystron frequency is swept with a 10-Hz sawtooth. About 10 MHz is displayed. This double resonance signal is due to a populational effect in saturated regime.

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[1] M. Mizushima and P. Venkateswarlu, J. Chem. Phys. 21, 705 (1953).

[2] K. Uehara, K. Sakurai, and K. Shimoda, J. Phys. Soc. Jap. 26, 1018 (1969).

[3] A. C. Luntz and R. G. Brewer, J. Chem. Phys. 54, 3641 (1971).

[4] K. T. Hecht, J. Mol. Spectrosc. 5, 355 (1960); J. Mol. Spectrosc. 5, 390 (1960).

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

[6] W. L. Barnes, J. Susskind, R. H. Hunt, and E. K. Plyler, J. Chem. Phys. 56, 5160 (1972).

[7] A. J. Dorney and J. K. G. Watson, J. Mol. Spectrosc. 42, 135 (1972).

[8] J. T. Hougen (private communication).

[9] H. J. Gerritsen and S. A. Ahmed, Phys. Lett. 13, 41 (1964).

[10] K. Shimoda, Paper S1, Digest of Technical Papers, VII IQEC Conference, Montreal, May 1972.

[11] S. M. Freund and T. Oka, Appl. Phys. Lett. 21, 60 (1972).

[12] R. L. Barger and J. L. Hall, Phys. Rev. Lett. 22, 4 (1969).

[13] J. L. Hall (private communication).

[14] F. Shimizu, Chem. Phys. Lett. 17, 620 (1972).