Double Resonance Spectra Involving Torsional Excited Levels and CO Stretch Band Transitions of CD_3OH

Sung-Eul CHOI

Department of Physics, University of Inchon, Inchon 402-749, Korea

Infrared-Radio frequency double resonance (IRRFDR) and Infrared-Microwave double resonance (IRMWDR) spectroscopy have been used to probe a level of A symmetry for CD_3OH. Double resonance spectra of CD_3OH have been investigated over the range of 940 to 1020 cm^{-1}. Twenty K-type doublet transitions have been observed in both the radio frequency region, which covers 50 MHz to 1 GHz, and the microwave region, which covers 8 GHz to 12 GHz. The results propose new assignments of infrared (IR) absorption transitions and far-infrared (FIR) laser emission lines. These involve torsional excited levels and CO stretch states. Measurements of the A state splitting have permitted the determination of the asymmetry splitting parameters $S^o(n, K)$ and $S^o(n, K)$ for $(n, K)=(0, 3)$ and (1, 3).

I. INTRODUCTION

Due to the successful use of methanol and its isotopomers in optically pumped FIR lasers, they have attracted a great interest from spectroscopists. These are one of the simplest asymmetric top molecules exhibiting internal rotation.

Over the past decade several different techniques have been used to ravel the complicated spectra of these molecules in the IR region of the spectrum. The techniques include Fourier-transform[1,2] and diode-laser spectrometers[3] for high resolution absorption spectroscopy. The observation and frequency measurement of optically pumped FIR laser lines and the use of double resonance techniques have been an important aid in the analysis of the congested CO stretch band.

The CO stretch band of methanol and its isotopomers is well overlapped with CO_2 laser emission lines in the 10 μm region. The 10 μm absorption region of the CD_3OH molecule have been studied using diode laser spectroscopy.[3,4] By pumping several of the isotopic species, researchers have reported many hundred FIR laser lines from these species.[5] The study of CD_3OH molecules has not been made as extensively as in CH_3OH molecules. FIR laser lines, produced with the CD_3OH species, were first observed by Dyubko et al. in 1975.[6]

In the review of CD_3OH by Kon et al.[7] CD_3OH was ranked as the molecule giving rise to the second largest number of FIR laser lines (115 lines) next to the CH_3OH (331 lines at that time). Since then, many new CD_3OH FIR laser lines have been observed by Sigg et al.,[8] Pereira et al.,[9] and Saykally et al.[10] In 1987, Carelli et al.[11] re-investigated CD_3OH and found new FIR laser lines from this molecule by using a wave guide $^{12}C^{16}O_2$ laser with a frequency tunability of about 300 MHz around each laser line center. The larger tunability allowed for the observation of many new FIR laser lines with pump offsets outside the tuning range of conventional $^{12}C^{16}O_2$ lasers. The pump offset was measured accurately using the transferred-Lamb-dip technique. This group observed 108 new FIR laser lines ranging from 41.46 to 1155.5 μm. They measured the pump offset of 147 FIR laser lines. The total number of reported FIR laser lines is now approximately 340.[11,12] These substantial additions to the list of FIR lines, in connection with accurate frequency measurements and assignments of a number of these lines, has added to the understanding of the IR spectra of this molecule.

In spite of the large number of known CD_3OH FIR

laser lines, no FIR transitions has been assigned until 1983. One reason for this is that a Fermi resonance is significant in this part of the spectrum. Weber et al.[3] has identified the presence of a Fermi resonance between pure CO stretch-state levels and torsional-excited levels of the ground state. Fermi resonance is a perturbation occurring for energy levels of nearly the same energy and results from the interactions between different vibrations of the same symmetry and the same rotational quantum numbers. As a consequence some energy levels are shifted thus making assignments more complicated. The stretch band is a parallel band, which displays the conventional P, Q, and R branch structure. This band was studied by Woods[1] who assigned rotational quantum numbers J to the spectral lines. In 1982, Weber and Maker,[3] reported assignments of the intramultiplet structure of the P and R multiplets for CD_3OH using diode laser spectra. They provided molecular constants for the CO stretch state. In their analysis, they pointed out that there was a significant Fermi resonance between the torsional ground state ($n=0$) of the CO stretch and the excited vibrational state. This Fermi resonance was used to explain the discrepancy between a pump $^{12}C^{16}O_2$ laser frequency and an expected infrared absorption transition frequency.

Six FIR laser lines from CD_3OH pumped by the 10R36 and 10R18 $^{12}C^{16}O_2$ laser lines have been assigned to specific rotational energy levels in the excited CO stretch band.[13] Partial assignments of seven FIR laser lines pumped by $^{13}C^{16}O_2$ 9R34, $^{12}C^{16}O_2$ 10P18, and $^{12}C^{16}O_2$ 10P22 were discussed by Mukhopadhyay et al.[14] Mukhopadhyay et al.[15] confirmed several assignments of IR pump and FIR emission transitions by using high resolution Fourier transform spectra and frequency combination relations for closed IR/FIR transition loops. Fermi resonance was also used in their analysis.

The internal hindered rotation of the methyl group with respect to the hydroxyl group makes the spectrum complex. Therefore assignments have in the past strongly relyed on laser-based labeling techniques. Among these are the IRRFDR and IRMWDR techniques. Double resonance spectra, associated with the CO stretch band of CD_3OH, have been investigated over the range of 940 cm^{-1} to 1020 cm^{-1}. Most of the P and R branch lines of the CD_3OH molecule are

located around the Q branch origin at 985.53 cm^{-1}.[16] This frequency range has been studied using the 10P and 10R branch lines of $^{12}C^{16}O_2$, the 10P and 10R branch lines of $^{12}C^{18}O_2$, and the 9P branch lines of $^{13}C^{16}O_2$ laser. All of these branches overlap the CO stretch band of CD_3OH. A systematic search on these laser lines have been made in this experiment.

II. EXPERIMENTAL

The detailed experimental setup for IRRFDR can be found elsewhere[17]. The experimental setup for IRMWDR is shown in Fig. 1. The IRMWDR setup is composed of three essential parts; the semisealed CO_2 laser, the radio frequency sweep oscillator, and the X-band microwave absorption cell. The frequency ranges covered in this experiment were 50 MHz~1 GHz with the IRRFDR technique and 8 to 12 GHz with the IRMWDR technique. This microwave region was limited by the equipment. The same sweep oscillator as used in the RF experiments was used except that the RF plug-in unit was replaced by a microwave plug-in unit. Using the RF absorption cell in the microwave region was possible since the transmission varied greatly with the frequency.[18] Instead, an X-band microwave absorption cell was used. The design of the microwave absorption cell is shown in Fig. 2.

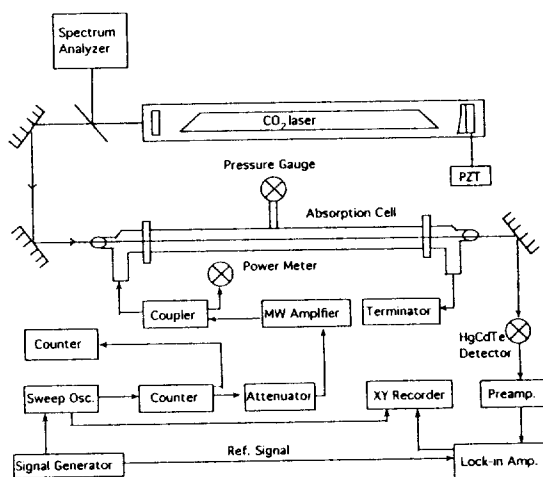The cell is 1 m long, and has E bends mounted

Fig. 1. Experimental setup for the infrared-radio frequency double resonance experiment.
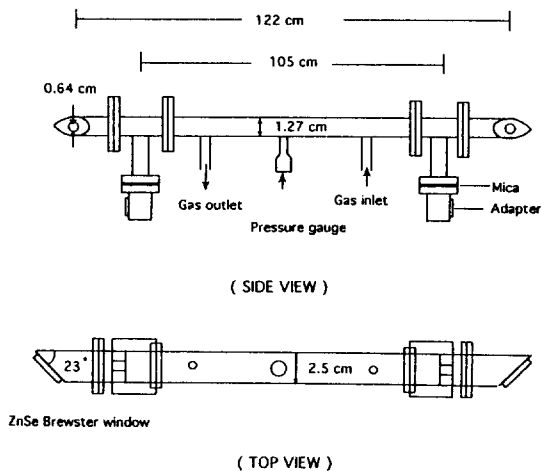
Fig. 2. The infrared-microwave absorption cell.

Fig. 3. Infrared-radio frequency double resonance signals in CD_3OH observed with the 9P20 line of the $^{13}C^{16}O_2$ laser. The laser power was 700 mW, the radio frequency power was 300 mW, and the sample pressure was 180 mTorr. A time constant of 300 msec was used. Amplifier sensitivity was 50 μV.

at both ends. Using this cell, the microwave could be coupled in at one end and out of the other end without reflections, and the microwave power could be measured after a single pass of the cell. A 6 mm hole was drilled in each E bend, for in-coupling and out-coupling of the laser radiation. The appropriate holes were sealed with mica windows and ZnSe Brewster windows for maximum transmission of microwave and infrared radiation, respectively.

The microwave frequency was slowly swept from 8 to 12 GHz in four 1 GHz steps, each sweep taking 120 seconds. Once a signal was observed a signal region around the signal (± 50 MHz) was recorded, and the frequency was measured using a counter. The other experimental apparatus and procedures were the same as in the IRRF experiment.[17] The sample used throughout this work was CD_3OH (isotopic purity of 99% atom % D), which was obtained from Aldrich Chemicals. The above technique was applied to the CD_3OH sample, using three isotopic derivatives $^{12}C^{16}O_2$, $^{12}C^{18}O_2$, and $^{13}C^{16}O_2$ in the pump laser.

III. RESULTS AND ANALYSIS

Twenty double resonance signals were observed using one $^{13}C^{16}O_2$ and eight $^{12}C^{16}O_2$ laser lines. Some of the experimental results are shown in Fig. 3 and 4.
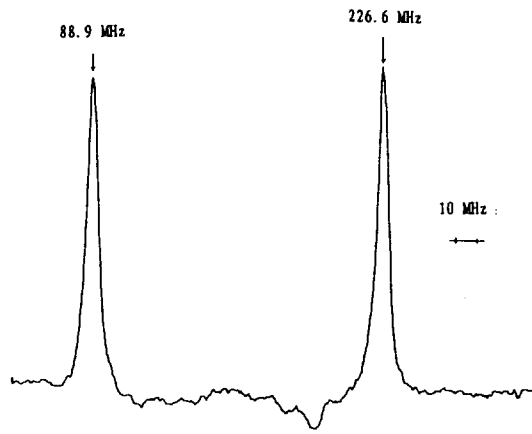
The measured frequencies are listed in Table 1 and

Fig. 4. Infrared-microwave double resonance signals in CD_3OH observed with the 10P6 line of the $^{12}C^{16}O_2$ laser. The laser power was 1050 mW, the microwave power was 2760 mW, and the sample pressure was 90 mTorr. A time constant of 300 msec was used. Amplifier sensitivity was 50 μV.
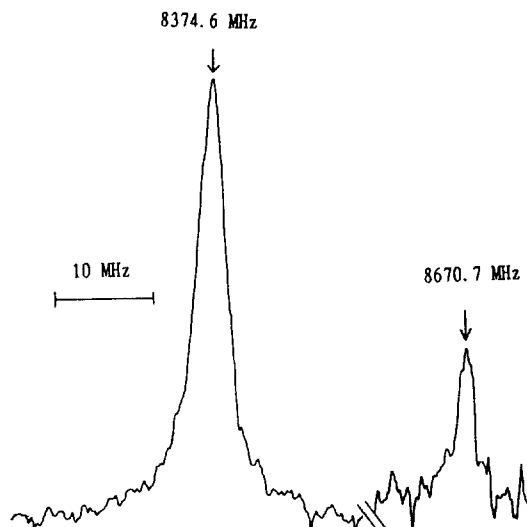
Table 1. Observed infrared-radio frequency double resonance signals of CD_3OH

CO_2 laser line	Frequency[a] (MHz)	Relative intensity[b]
$^{12}C^{16}O_2$		
10R14	129.5(4)	M
	297.0(3)	M
10R16	294.5(3)	M
$^{13}C^{16}O_2$		
9P20	88.9(3)	VS
	226.6(5)	VS

[a]: Figures in parentheses indicate the standard deviation in the least-significant figure.

[b]: Relative intensities according to the ratio of signal to noise as follows; VS: s/n>100, M: 20>s/n>10.

Table 2. Observed infrared- microwave double resonance signals of CD_3OH

CO_2 laser line	Frequency[a] (MHz)	Relative intensity[d]
$^{12}C^{16}O_2$		
10P6	8374.6(6)	S
	8670.7(5)	W
10P8	8887.4(4)[b]	S
	8889.4(2)[b]	S
	8910.9(5)[b]	M
	8937.1(2)[c]	S
10P16	8038.6(2)	VS
	8917.8(2)	VS
10R14	8189.3(3)	W
	10211.8(3)	M
	10416.6(2)	M
10R20	8115.0(7)	VW
	8691.0(2)	VW
10R38	8048.3(4)	M
	10473.2(2)	S

[a]: Figures in parentheses indicate the standard deviation in the least-significant figure.

[b]: The microwave frequency at a positive offset.

[c]: The microwave frequency at a negative offset.

[d]: Relative intensities according to the ratio of signal to noise as follows; VS: s/n>100, S: 100>s/n>20, M: 20>s/n>10, W: 10>s/n>5, VW: 5>s/n>2.

Table 2, together with the relative intensities of the signals. All double resonance signals were recorded by sweeping the radio frequency and microwave fre-

quency, while maintaining the infrared frequency at the absorption line center. No double resonance signals were observed when using the $^{12}C^{18}O_2$ laser.

Four quantum numbers are needed to label the energy levels of methanol and its isotopomers. Here we used the notation $\Delta(n \tau K, J)^\tau$, where n is the torsional quantum number and τ can take on values of 1, 2, and 3 and was used to characterize the threefold hindering potential. The quantum number K is the component along the a-internal axis of the total angular momentum specified by the quantum number J. Torsion-rotation levels are grouped into E_1, A, and E_2, corresponding to $\tau + K = 3N$, $3N+1$, and $3N+2$, respectively, where N is an integer. Only A states can exhibit asymmetry splitting, and hence the E_1 and E_2 levels remain twofold degenerate. The A states with $K \neq 0$ split into A^- and A^-, where the splitting increases with J and decreases rapidly with K.

Asymmetry splitting of the levels of A symmetry can be expressed in the form[19]

$$\Delta(n \tau K, J) = S(n \tau K, J) \frac{(J+K)!}{(J-K)!} \qquad (1)$$

where $S(n \tau K, J)$ can be evaluated by the perturbation theory to the Kth order. In order to fit experimental data, it is often necessary to add higher order terms to this expression.[20,21] However, we applied Eq. (1) because of the limited data set.

The energies of the torsion-rotation levels of CD_3OH were calculated using the published molecular parameters.[22,23,24] The energies were calculated for both the ground state and the CO stretch state using an existing computer program.[25] Some of the parameters for the CO stretch state are not known yet. Therefore we have used ground state values for the unknown excited state parameters. Experience from work on other isotopomers indicate that this is justified since the CO stretch parameters are usually quite similar to those for the ground state and in any case they count for only a small fraction of the total energy. Asymmetry parameters, including new values calculated from the results of the present work, are given in Table 3.

1. IRRFDR Spectra from CD_3OH Using the $^{13}C^{16}O_2$ 9P20 Pump Line

Strong double resonance signals were observed at

Table 3. Asymmetry splitting parametrs of CD_3OH

S(n,K)	ground (MHz)[a]	CO stretch (MHz)[a]
S(0,1)	289.99[b]	328.13[b]
	256.17(24)[c]	292.92(24)[c]
S(0,2)	0.2013[b]	0.2628[b]
S(0,3)	$4.1148(138) \times 10^{-5(d)}$	$6.2881(138) \times 10^{-5(d)}$
	$4.9542 \times 10^{-5(b)}$	$5.2623 \times 10^{-5(b)}$
S(0,4)	$2.7517 \times 10^{-9(b)}$	$4.6830 \times 10^{-9(b)}$
S(1,3)	$8.9472(5) \times 10^{-5(d)}$	$1.1522(1) \times 10^{-4(d)}$

[a]: Figures in parentheses indicate the standard deviation in the least-significant figure.
[b]: Calculated from the molecular parameters.
[c]: Taken from Weber et al.[4]
[b]: Calculated from the results of this work

88.9 MHz and 226.6 MHz. So far, no FIR laser emission lines have been observed with this pump line. The Fourier transform spectra of CD_3OH by Wood[1] indicate that there is strong absorption in the R (11) multiplet at 1000.698 cm⁻¹, which is in close coincidence with the laser line at 1000.64725 cm⁻¹. Since the K splitting increases with J, the 226.6 MHz line corresponds to $J=12$ in the vibrational CO stretch state, and the 88.9 MHz line to $J=11$ in the vibrational ground state. Using eq. (1) and taking into consideration the order of the theoretical values of S(n, K) in Table 3, the most probable value set for (n, K) is (0, 3). Then, since K-splitting only occurs in A⁻states (for which $\tau+K=3N+1$, N being an integer), the only possible value of τ is 1. The CO stretch vibrational motion is parallel to the a-axis and only vibrational transitions with $\Delta K=0$ are allowed. The infrared transition is tentatively assigned to the $^QR(0\ 1\ 3,\ 11)$ transition, and is shown in Table 4. Using molecular parameters from Weber and Maker[3,4] the infrared transition frequency

can be calculated to be 1000.6672 cm⁻¹ which is in good agreement with the Wood's measurements,[1] considering that the maximum J value in the former study was 8. The IR absorption transition can be either case (a) (013⁻, 11)ᵛ→(013⁺, 12)ᵛ′, or case (b) (013⁻, 11)ᵛ→(013⁻ 12)ᵛ′. The assignments of IR and RF transitions are given in Table 4.

Theoretical values for $S^v(0, 3)$ and $S^w(0, 3)$, calculated using the constants of Lees et al.,[22] are compared with the values obtained in the present work in Table 3. From our assignment of the IR absorption transition we could predict FIR emission transitions which should be observed when pumping with the $^{13}C^{16}O_2$ 9P20 laser line. These are either case: (a) (013⁻, 12)ᵛ→(013⁺, 11)ᵛ′, (013⁺, 12)ᵛ→(022⁻, 12)ᵛ′, and (013⁺, 12)ᵛ→(022⁺, 11)ᵛ′ transitions; or (b) (013⁻, 12)ᵛ→(013⁻, 11)ᵛ′, (013⁻, 12)ᵛ→(022⁺, 12)ᵛ′, and (013⁻, 12)ᵛ→(022⁻, 11)ᵛ′ transitions. The corresponding frequencies are 15.56 cm⁻¹ (∥), 0.58 cm⁻¹ (⊥), and 16.13 cm⁻¹ (∥), respectively. These are summerized in Table 5. The infrared and FIR transitions involved in this scheme are shown in Fig. 5. In these calculations we have not taken asymmetry splitting into consideration. It should also be mentioned that the 0.58 cm⁻¹ line is too low in frequency to be observed in a FIR laser. As expected, these three FIR lines constitute a triad.

2. IRMWDR Spectra from CD_3OH Using the $^{12}C^{16}O_2$ 10P6 Pump Line

Two IRMWDR signals were observed at 8374.8 MHz and 8670.7 MHz. Comparisons between the Fourier transform data[1] and the $^{12}C^{16}O_2$ 10P6 laser frequency at 956.18498 cm⁻¹ show that this laser frequency lie between the P (21) multiplet at 956.843 cm⁻¹ and the P (22) multiplet at 955.415 cm⁻¹. It is expected that

Table 4. Assignment of infrared absorption, radio frequency and microwave transitions for CD_3OH

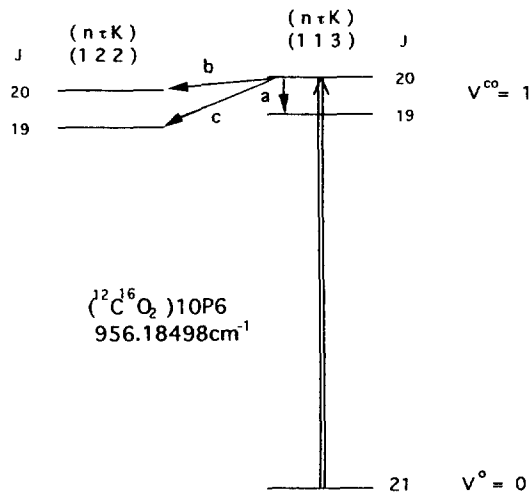| CO_2 laser line (cm⁻¹)[a]	Infrared absorption transition	Frequency (MHz)[b]	RF and MW transition (nτK, J)
$^{13}C^{16}O_2$ 9P20	$^QR(0\ 1\ 3^{\pm}\ ,\ 11)$	88.9(3)	(0 1 3⁻, 11)ᵛ
(1000.64725)		226.6(5)	(0 1 3⁺, 12)ᵛ′
$^{12}C^{16}O_2$ 10P6	$^QP(0\ 1\ 3^+,\ 21)$	8374.8(6)	(1 1 3⁺, 20)ᵛ′
(956.18498)		8670.7(5)	(1 1 3⁺, 21)ᵛ

[a]: Taken from Freed et al.[26]
[b]: Figures in parentheses indicate the standard deviation in the least significant figure.

Table 5. Assignment of FIR laser lines in CD_3OH

Pump line (cm^{-1})[a]	Pump Assignment	Far-Infrared Emission[b] (cm^{-1})	Emission Assignment[c] (n τK, J)[p]
$^{13}C^{16}O_2$ 9P20 (1046.85423)	$^QR(0\ 1\ 3,\ 11)$	15.56($\parallel$)	$(0\ 1\ 3^\pm,\ 12)^\infty \rightarrow (0\ 1\ 3^\pm,\ 11)^\infty$
		0.58($\perp$)	$\rightarrow (0\ 2\ 2^\mp,\ 12)^\infty$
		16.13($\parallel$)	$\rightarrow (0\ 2\ 2^\pm,\ 11)^\infty$
$^{12}C^{16}O_2$ 10P6 (956.18498)	$^QP(1\ 1\ 3,\ 21)$	25.84($\parallel$)	$(1\ 1\ 3^\pm,\ 20)^\infty \rightarrow (1\ 1\ 3^\pm,\ 19)^\infty$
		70.72($\perp$)	$\rightarrow (1\ 2\ 2^\mp,\ 20)^\infty$
		96.54($\parallel$)	$\rightarrow (1\ 2\ 2^\pm,\ 19)^\infty$

[a]: Taken from Freed et al.[26]
[b]: Predicted FIR laser lines from this work.
[c]: Predicted FIR transitions from this work.
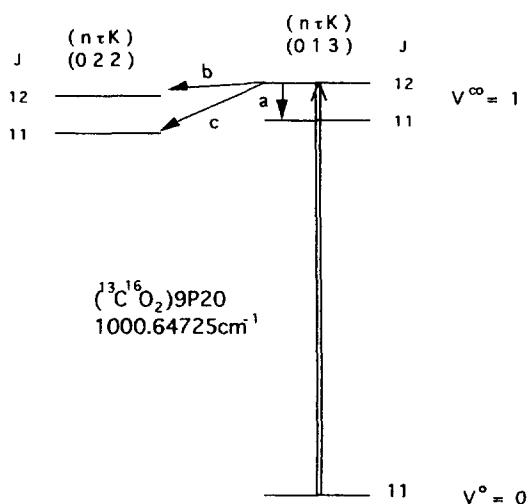
a : 15.56 cm^{-1}($\parallel$)

b : 0.58 cm^{-1}($\perp$)

c : 16.13 cm^{-1}($\parallel$)

Fig. 5. Energy-level scheme of CD_3OH showing the transition pumped by the 9P20 $^{13}C^{16}O_2$ laser line and three predicted FIR emission transitions.

a : 25.84 cm^{-1}($\parallel$)

b : 70.72 cm^{-1}($\perp$)

c : 96.54 cm^{-1}($\parallel$)

Fig. 6. Energy-level scheme of CD_3OH showing the transition pumped by the 10P6 $^{12}C^{16}O_2$ laser line and three predicted FIR emission transitions in the torsional levels.

the lower of the two microwave frequencies corresponds to an asymmetry splitting in the excited state while the other is a transition in the ground state. For K≤4 there are no coincidences between the laser line and the $n=0$ transitions in the molecule. Therefore we tentatively assign the transition to an $n=1$ transition, due to the relatively large signal to the noise ratio of the signal. By applying eq. (1), however, it

is found that a transition with $(J,\ K)=(21,\ 3)$ is the most probable. Therefore we tentatively assign the absorption transition as either the $(1\ 1\ 3^+,\ 21)^v \rightarrow (1\ 1\ 3^+,\ 20)^v$ transition or the $(0\ 1\ 3^-,\ 21)^v \rightarrow (1\ 1\ 3^-,\ 20)^{v\infty}$ transition. The assignment of IR and MW absorption transitions is given in Table 4. From this assignment, we obtained the asymmetry splitting parameters $S^v(1,\ 3)=8.9472(50) \times 10^{-5}$ MHz for the ground state

and $S^{\omega}(1, 3) = 1.1522(1) \times 10^{-4}$ MHz for the CO stretch state. FIR emission transitions can be predicted from the assignment of the IR absorption transition. These are either: case (a) $(1\ 1\ 3^+, 20)^{\omega}$ $(1\ 1\ 3^+, 19)^{\omega}$, $(1\ 1\ 3^-, 20)^{\omega} \rightarrow (1\ 2\ 2^-, 20)^{\omega}$, and $(1\ 1\ 3^+, 20)^{\omega} \rightarrow (1\ 2\ 2^+, 19)^{\omega}$ transitions; or case (b) $(1\ 1\ 3^-, 20)^{\omega} \rightarrow (1\ 1\ 3\ , 19)^{\omega}$, $(1\ 1\ 3^-, 20)^{\omega} \rightarrow (1\ 2\ 2^+, 20)^{\omega}$, and $(1\ 1\ 3^-, 20)^{\omega} \rightarrow (1\ 2\ 2^-, 19)^{\omega}$ transitions. The corresponding frequencies are 25.84 cm^{-1}(‖), 70.72 cm^{-1} (⊥), and 96.54 cm^{-1}(‖), respectively. The predicted FIR laser assignment is summerized in Table 5. The infrared and FIR transitions involved in this scheme are shown in Fig. 6. In these calculations we have not taken asymmetry splitting into consideration. These three FIR lines constitute a triad.

IV. CONCLUSIONS

IRRFDR and IRMWDR techniques have been used to probe a level of A symmetry for CD_3OH. Double resonance spectra of CD_3OH have been investigated over the range of 940 to 1020 cm^{-1}. Twenty K-type doublet transitions have been observed in both the radio frequency region of 50 MHz to 1 GHz and the microwave region of 8 GHz to 12 GHz. From the the results of this work, we could assign two infrared (IR) and four RF and MW absorption transitions. Also, we predicted six FIR emission transitions from the two IR absorption assignments. These involve torsional excited levels and CO stretch states. The new obtained values of asymmetry splitting parameters for the torsional ground states are $S^{\nu}(0, 3) = 4.1148 \times 10^{-5}$ MHz and $S^{\omega}(0, 3) = 6.2881 \times 10^{-5}$ MHz and those for the torsional excited states are $S^{\nu}(1,3) = 8.9472 \times 10^{-5}$ MHz and $S^{\omega}(1, 3) = 1.1522 \times 10^{-4}$ MHz.

REFERENCE

[1] D. R. Woods, Ph. D. Dissertation, Univ. of Michigan, Ann Arbor (1970).

[2] I. Mukhopadhyay, M. Mollabashi, R. M. Lees, J. W. C. Johns, J. Mol. Spectrocs. **138**, 521 (1989).

[3] W. H. Weber, P. D. Maker, J. Mol. Spectrosc. **93**, 131 (1982).

[4] W. H. Weber, D. H. Leslie, C. W. Peters, J. Mol. Spectrosc. **89**, 214 (1981).

[5] K. J. Button, M. Inguscio, and F. Strumia, eds., *Review of Infrared and Millimeter Waves* (Plenum, New York, 1984), Vol. 2.

[6] S. F. Dyubko, V. A. Svich, and L. D. Fesenko, Izv. Radiofisika, **18**, 1434 (1975).

[7] S. Kon, T. Kachi, Y. Tsunawaki, and M. Yamanaka, In *Review of Infrared and Millimeter Waves*, ed. K. J. Button, M. Inguscio, F. Strumia, Vol. 2(Plenum, New York 1984) 159.

[8] H. Sigg, H. J. A. Bluyssen, and P. Wyder, IEEE J. Quantum Electron., **QE-20**, 616 (1978).

[9] D. Pereira, C. A. Ferrari, and A. Scalabrin, Int. J. M. M. Waves, **7**, 1241 (1986).

[10] R. J. Saykally, K. M. Evenson, D. A. Jennings, L. R. Zink, and A. Scalabrin, Int. J. IR. M. M. Waves, **8**(6), 653 (1987).

[11] G. Carelli, N. Ioli, A. Moretti, D. Pereira, and F. Strumia, Appl. Phys., **B44**, 111 (1987).

[12] S. Kon, T. Kachi, Y. Tsunawaki, Y. Yamanaka, In *Review of Infrared and Millimeter Waves*, ed. by K. J. Button, M. Inguscio, F. Strumia, Vol.2 (Plenum, New York 1984) 159.

[13] T. Kachi and S. Kon, Int. J. M. M. Waves, **4**(5), 767 (1983).

[14] I. Mukhopadhyay, R. M. Lees, and J. Lewis Bevan, Int. J. IR. M. M. Waves, **9**(6) 545 (1988).

[15] I. Mukhopadhyay, M. Mollabashi, R. M. Lees, and J. W. C. Johns, J. Mol. Spectrosc., **138**, 521 (1989).

[16] M. C. L. Gerry, R. M. Lees, and G. Winnewisser, J. Mol. Spectrosc., **61**, 231 (1976).

[17] S. E. Choi, to be published in J. Kor. Phys. Soc. **28**(4) 1995. 8.

[18] H. Dreizler, W. Schrepp, and R. Schwarz, Z. Naturforsch, **34a**, 571 (1979).

[19] E. V. Ivash and D. M. Dennison, J. Chem. Phys. **21**, 1804 (1953).

[20] E. Arimondo, M. Inguscio, A. Moretti, M. Pellegrino, F. Strumia, Opt. Lett. **5**, 496 (1980).

[21] H. O. Henningsen and J. C. Petersen, J. Opt. Soc. Am. **B 5**, 1848 (1988).

[22] R. M. Lees and J. G. Baker, J. Chem. Phys., **48** (12), 5299 (1969).

[23] Y. Y. Kwan and D. M. Dennison, J. Mol. Spectrosc., **43**, 291 (1972).

[24] R. H. Hughes, W. E. Good, and D. K. Coles, Phys. Rev. **84**, 487 (1951).

[25] S. E. Choi, Ph. D. Dissertation, University of Alabama, Tuscaloosa, AL, (1991).

[26] C. Freed, L. C. Bradley, and R. G. O'Donnell, IEEE J. Quantum Electron., **QE-16**, 1195 (1980).