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# NEW FIR LASER LINES AND FREQUENCY MEASUREMENTS FOR OPTICALLY PUMPED $CD_3OH$

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Twenty new cw FIR laser lines in $CD_3OH$, optically pumped by a $CO_2$ laser, are reported. The frequencies of 39 of the stronger laser lines were measured relative to stabilized $CO_2$ lasers with a fractional uncertainty, as determined by the reproducibility of the FIR frequency itself, of 2 parts in $10^7$.

Key Words: $CD_3OH$ laser lines, laser frequency measurements, optically pumped FIR laser, new laser lines, relative intensity, relative polarization.

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## Introduction

The set of isotopes of methyl alcohol - $CH_3OH$, $CD_2OH$, $CH_3OD$, $CH_2DOH$, $CHD_2OH$, and $^{13}CH_3OH$ - occupies a prominent position in the list of cw optically pumped far infrared (FIR) lasing molecules, accounting for approximately 35% of all the presently tabulated lasing lines (1). Even more important is the fact that these isotopes are responsible for about 130 of the approximately 160 lines found at wavelengths shorter than 200 μm. Hence, this series of isotopes alone constitutes the majority of all of the frequency coverage needed for frequency metrology and laser spectroscopy in this region of the FIR. This laboratory has been carrying out a program to systematically measure frequencies of known methanol lasing transitions and to search for new FIR laser lines. The results of frequency measurements, accurate to a few parts in $10^7$, have been published for $CH_3OH$, $CH_3DOH$, and $CD_3OD$ (2 - 4). In this paper we report similar measurements on 39 of the stronger lasing transitions in $CD_3OH$ (methanol-$d_3$).

The first account of optically-pumped FIR lasing action in $CD_3OH$ was published by Dyubko et al. (5) who found 70 cw transitions ranging from 180 to 1300 μm. Subsequently, Danielewicz and Weiss (6) reported finding 21 new cw lines at shorter wavelengths, Grinda and Weiss (7) found another 10 new lines, Yoshida et al. (8) found 7 new lines, Sigg et al. (9) found a number of new short wavelength lines, and Pereira et al. (10) found 69 new lines, many of them at long wavelengths. In all cases, a $CO_2$ laser was used to pump a conventional hole-coupled Fabry-Perot FIR resonator, and wavelengths were measured with an accuracy of about 0.5%. At 100 μm this corresponds to an uncertainty of 15 GHz in the laser frequency, which is entirely too crude for applications in frequency synthesis or spectroscopy. The frequency measurements reported in this paper correspond to over a thousandfold improvement in accuracy over the wavelength determinations.

## Experimental

The $CD_3OH$ lines were pumped by a 3 m, invar-stabilized, grating- and piezoelectrically-tuned $CO_2$ laser having single line cw powers of up to 30 w. The

$CO_2$ laser power was coupled into a Fabry-Perot resonator ($R_1$ = 200 cm, $R_2$ = ∞, D = 100 cm) by focusing the beam through a 1 mm diameter hole in the center of the curved 12.5 cm diameter gold-coated copper mirror with 1 m focal length optics. FIR power was coupled out of the resonator with a 3 mm hole located 5.5 mm from the center of the same mirror. The position of the flat mirror at the other end of the cavity was adjusted with a micrometer drive to change the resonant frequency of the cavity. Irises in front of each mirrors were used to discriminate against higher order modes. Wavelengths of the laser lines accurate to ± 0.1 µm were measured by counting the number of modes over a 5 mm scan, using the known wavelength of the 118.8 µm line of $CH_3OH$ for calibration. This level of accuracy was needed to predict the lasing frequency to within the 1500 MHz detection bandwidth.

For the frequency measurements, the FIR laser output was focused onto a long-wire (6 mm), W-Ni, point-contact diode. The angle between the beam and the wire was adjusted to maximize the coupling. FIR frequencies were synthesized with two $^{12}C^{16}O_2$ lasers and an X-band klystron, as described previously (11). Each $CO_2$ laser was actively stabilized to the standing-wave saturation resonance in a low-pressure (5.3 Pa), intracavity, $CO_2$ absorption cell (12). The X-band klystron was stabilized to a quartz crystal, and its frequency was counted. The uncertainty in this synthesized FIR frequency was less than 100 kHz. The beat frequency between the synthesized frequency and the FIR laser frequency was amplified (25 db) and measured with a 1500-MHz spectrum analyzer and marker oscillator.

## Results

In Table I, we reported 20 new laser lines from a $CD_3OH$ sample of 99% isotopic purity. We have listed all of the lines reported in References (6) and (7) and those that oscillate in our laser from ref. (8), (9), and (10). Because of the same purity problems mentioned in Ref. (5), we have listed only those lines from that source which we could reproduce with our apparatus. Polarization of the FIR radiation relative to that of the $CO_2$ pump radiation was measured for about two-thirds of the listed lines.

Frequency measurements made for 39 lasers lines of $CD_3OH$ are presented in Table II. The vacuum wavenumber is derived from the measured frequencies with c=299 792 458 m/s (13). Pressures given in the table for the various lines were measured with an air-calibrated thermocouple gauge and correspond to the maximum in the FIR laser output power. Polarizations of the lines relative to the linearly-polarized $CO_2$ pump laser were measured with an external metal-mesh polarizer. Relative powers of the lines were determined by monitoring the laser output with a diamond window Golay cell with a 0.24-mm-thick crystal-quartz filter to block the $CO_2$ radiation. Other calibrated attenuators were used with strong lasing lines to prevent saturation of the detector. Relative powers in Table I correspond to the maximum output of each line and are labelled only VS, S, M, W, or VW because the actual intracavity power varies with coupling, wavelength, and pump power, and no attempt was made to ascertain these dependencies.

## Discussion of Results

The estimated fractional frequency uncertainty of about $\pm 2 \times 10^{-7}$ results from a combination of factors. Principally, the accuracy is limited by our ability to set the free-running FIR laser to the center of its unperturbed gain-profile. This problem is compounded by shifts caused by competing lines and modes as well as by splittings and symmetries introduced into the lineshape by the ac-Stark and anisotropic-gain effects (14, 15). Variations up to several megahertz from these effects have occurred in past measurements but can usually be reduced by up to a factor of ten with great care in the measurement. Pressure shifts are small and are difficult to observe over the normal operating pressure range of the FIR laser.

Finally, we note that the 39 $CD_3OH$ measured frequencies in this work are those for lines that oscillated easily in our system. Seventeen of these lines are reported here for the first time; the 22 others were observed in the earlier work. Of the 70 cw lines reported in Ref. (5), we find only 13 that oscillate in our apparatus; all lines reported in References (6) and (7) were observed. In addition, we were able to separate the $R_I(34)$ pump frequency into three separate offsets with the use of a FIR laser transversely pumped to eliminate frequency jumping at the ends of the tuning curve of $CO_2$ caused by $CO_2$ laser radiation feedback.

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TABLE I. $CD_3OH$ Lasing Lines Arranged by Pump

| $CO_2$ Pump Line | $CD_3OH$ Laser Line $\lambda(\mu m)$ | Relative Polarization | $CD_3OH$ Power | Ref. |
|---|---|---|---|---|
| 9.4 Band | | | | |
| $R_{II}(34)$ | 54.0 | $\perp$ | VS | 7 |
| | 60.8 | $\|$ | VS | 7 |
| $R_{II}(28)$ | 40.0 | - | - | new |
| | 49.8 | $\perp$ | VS | 7 |
| | 55.6 | $\perp$ | | new |
| | 159.4$^a$ | $\|$ | S | 7 |
| | 181.7$^a$ | $\|$ | M | 8 |
| | 370.5$^a$ | $\|$ | M | 5 |
| $R_{II}(26)$ | 50 | $\perp$ | - | new |
| | 498.7 | - | - | new |
| $R_{II}(22)$ | 583 | $\|$ | W | 5,7 |
| $R_{II}(14)$ | 120.7$^a$ | $\|$ | M | 8 |
| | 182.6$^a$ | $\perp$ | M | 7 |
| | 236 | $\|$ | M | 7 |
| | 352.5$^a$ | $\|$ | M | 7 |
| $R_{II}(6)$ | 35.5 | $\|$ | W | new |
| | 48.4 | $\perp$ | M | 9 |
| | 56.9 | $\perp$ | W | 7 |
| $P_{II}(8)$ | 223 | $\perp$ | W | 7 |
| $P_{II}(28)$ | 435 | $\perp$ | VW | 7 |
| $P_{II}(32)$ | 351 | $\|$ | VW | 7 |

Table I (Continued)

| | | | | |
|---|---|---|---|---|
| $P_{II}(36)$ | 189.7$^a$ | $\parallel$ | S | 10 |
| $P_{II}(40)$ | 198.7$^a$ | $\parallel$ | M | 7 |
| | 286.2$^a$ | $\parallel$ | W | 5 |
| 10.4 μm Band | | | | |
| $R_I$ (45) | 68.8 | - | - | new |
| $R_I$ (38) | 50 | $\parallel$ | W | new |
| | 122.2$^a$ | $\perp$ | M | new |
| $R_I$ (36) | 253.7$^a$ | $\perp_d$ | S | 6 |
| | 418.7$^a$ | $\perp$ | M | 5,6 |
| $R_I^b$ (34)' | 43.1 | - | S | 9 |
| | 168.1$^a$ | $\perp$ | S | new |
| | 180.7$^a$ | $\perp$ | S | 6 |
| | 222.2$_a$ | $\perp$ | - | new |
| | 386.0$_a$ | $\perp$ | W | 10 |
| | 430.9$^a$ | $\perp$ | VW | 10 |
| $R_I^b$ (34)" | 86.7$^a$ | $\perp$ | M | 6 |
| | 264.8$^a$ | $\perp$ | M | 5,6 |
| $R_I^b$ (34)"' | 128.0$^a$ | $\perp$ | S | 6 |
| | 191.4$^a$ | $\parallel$ | M | 6 |
| $R_I$ (34)$^c$ | 37.6 | $\parallel$ | M | new |
| | 102.6 | $\perp$ | W | 6 |
| | 112.3 | $\perp$ | VW | 6 |
| | 498.0 | $\parallel$ | M | 6 |
| $R_I$ (32) | 131.6$^a$ | $\perp$ | M | new |
| | 165 | $\parallel$ | W | new |
| $R_I$ (30) | 67.5$^a$ | $\parallel$ | M | new |
| | 350 | $\perp$ | W | 5 |
| $R_I$ (28) | 310 | $\perp$ | W | 5 |
| $R_I$ (24) | 61.5 | - | VS | 9 |

Table I (Continued)

| | | | | |
|---|---|---|---|---|
| $R_I$ (18) | 41.5[a] | ⊥ | VS | 6 |
| | 43.7[a] | ∥ | VS | 6 |
| | 219 | ∥ | W | 6 |
| | 858.3[a] | ∥ | S | 5,6 |
| $R_I$ (16) | 81.6[a] | ∥ | W | 6 |
| | 86.4 | ⊥ | W | 6 |
| $R_I$ (14) | 136.6[a] | ∥ | W | new |
| | 389.1 | ∥ | VW | 10 |
| $R_I$ ( 8) | 41.5 | ⊥ | M | 6 |
| | 71.0[a] | ⊥[d] | M | 6 |
| | 203.3 | - | VW | new |
| | 553 | ∥ | - | 5 |
| | 646.5[a] | ∥ | W | 6 |
| $P_I$ (10) | 108.7[a] | ∥ | W | 10 |
| $P_I$ (18) | 144.1[a] | ∥ | S | 6 |
| | 287.3[a] | ∥ | S | 5,6 |
| | 290 | ⊥ | M | 6 |
| $P_I$ (22) | 34.8 | ∥ | M | 6 |
| | 40.1 | ⊥ | M | 6 |
| | 258.4[a] | ∥ | M | 5,6 |
| $P_I$ (24) | 238.3 | ⊥ | W | 6 |
| | 286.7[a] | ∥ | M | 5 |
| $P_I$ (28) | 190 | ∥ | W | new |
| | 276.7[a] | ∥ | M | 5 |
| $P_I$ (32) | 76.1 | ∥ | M | 6 |
| | 147.3[a] | ∥ | W | 10 |
| | 215.1[a] | ∥ | M | new |
| $P_I$ (42) | 76.3 | - | - | new |
| | 188.4[a] | ∥ | S | new |

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[a] Frequency measured

[b] Single, double, and triple primes indicate different pump offset frequencies.

[c] Other $R_I(34)$ pumped lines not observed in present experiment. Pump offset frequency not identified.

[d] Our measured polarization is opposite to that of Ref. (6).

TABLE II. Frequency measurements for 39 FIR lasing transitions of $CD_3OH$ (methanol-$d_3$) pumped by a $CO_2$ laser.

| $CD_3OH$ Laser Line λ (μm) | Measured Frequency[a] (MHz) | Vacuum Wavenumber[b] ($cm^{-1}$) | $CD_3OH$ Laser Press.[c] (Pa) | $CO_2$ Pump Line |
|---|---|---|---|---|
| 41.4 | 7 249 266.0 | 241.809 485 | 16 | $R_I$ (18) |
| 43.7 | 6 860 664.2 | 228.847 124 | 16 | $R_I$ (18) |
| 67.5 | 4 442 724.8 | 148.193 349 | 33 | $R_I$ (30) |
| 71.0 | 4 223 062.0 | 140.866 186 | 17 | $R_I$ ( 8) |
| 81.6 | 3 675 859.9 | 122.613 488 | 21 | $R_I$ (16) |
| 86.7 | 3 456 161.2 | 115.285 129 | 12 | $R_I$ (34)" |
| 108.7 | 2 758 781.7 | 92.023 051 | 20 | $P_I$ (10) |
| 120.7 | 2 484 584.9 | 82.876 831 | 40 | $R_{II}$(14) |
| 122.2 | 2 454 225.9 | 81.864 164 | 47 | $R_I$ (38) |
| 128.0 | 2 341 508.9 | 78.104 331 | 3 | $R_I$ (34)"' |
| 131.6 | 2 278 703.0 | 76.009 351 | 24 | $R_I$ (32) |
| 136.6 | 2 194 236.9 | 73.191 864 | 21 | $R_I$ (14) |
| 144.1 | 2 080 189.3 | 69.387 647 | 41 | $P_I$ (18) |
| 147.3 | 2 034 573.6 | 67.866 069 | 20 | $P_I$ (32) |
| 159.4 | 1 880 754.6 | 62.735 221 | 16 | $R_{II}$(28) |
| 168.1 | 1 783 601.1 | 59.494 527 | 4 | $R_I$ (34)' |
| 180.7 | 1 658 689.9 | 55.327 940 | 21 | $R_I$ (34)' |
| 181.7 | 1 649 830.3 | 55.032 415 | 16 | $R_{II}$(28) |
| 182.6 | 1 642 101.9 | 54.774 623 | 33 | $R_{II}$(14) |
| 188.4 | 1 591 053.2 | 53.071 823 | 23 | $P_I$ (42) |
| 189.7 | 1 580 101.8 | 52.706 524 | 40 | $P_{II}$(36) |
| 191.4 | 1 566 672.8 | 52.258 580 | 23 | $R_I$ (34)"' |
| 198.7 | 1 508 908.6 | 50.331 774 | 36 | $P_{II}$(40) |
| 215.1 | 1 393 856.9 | 46.494 060 | 21 | $P_I$ (32) |
| 222.2 | 1 349 100.1 | 45.001 136 |  | $R_I$ (34)' |
| 253.7 | 1 181 588.9 | 39.413 563 | 27 | $R_I$ (36) |
| 258.4 | 1 160 027.8 | 38.694 361 | 23 | $P_I$ (22) |
| 264.8 | 1 132 320.1 | 37.770 134 | 17 | $R_I$ (34)" |
| 276.7 | 1 083 395.1 | 36.138 170 | 20 | $P_I$ (28) |

Table II (Continued)

| $CD_3OH$ Laser Line λ (μm) | Measured Frequency[a] (MHz) | Vacuum Wavenumber[b] ($cm^{-1}$) | $CD_3OH$ Laser Press.[c] (Pa) | $CO_2$ Pump Line |
|---|---|---|---|---|
| 286.2 | 1 047 502.3 | 34.940 916 | 20 | $P_{II}(40)$ |
| 286.7 | 1 045 578.0 | 34.876 729 | 27 | $P_I$ (24) |
| 287.3 | 1 043 454.5 | 34.805 896 | 27 | $P_I$ (18) |
| 352.5 | 850 468.0 | 28.368 559 | 55 | $R_{II}(14)$ |
| 370.5 | 809 193.2 | 26.991 780 | 16 | $R_{II}(28)$ |
| 386.0 | 776 589.1 | 25.904 223 | 13 | $R_I$ (34)' |
| 418.7 | 715 987.6 | 23 882 776 | 15 | $R_I$ (36) |
| 430.9 | 695 691.5 | 23.205 772 |  | $R_I$ (34)' |
| 646.5 | 463 732.4 | 15.468 446 | 14 | $R_I$ ( 8) |
| 858.3 | 349 305.1 | 11.651 566 | 11 | $R_I$ (18) |

[a] The estimated fractional error in each measured frequency is $\pm 2\times10^{-5}$.

[b] Calculated from the measured frequency with c = 299 792 458 m/s.

[c] 133.3 Pa = 1 torr.