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# LASER LINES AND FREQUENCY MEASUREMENTS OF FULLY DEUTERATED ISOTOPOMERS OF METHANOL

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## ABSTRACT

Fully deuterated isotopomers of methanol ($^{12}CD_3OD$ and $^{13}CD_3OD$) were optically pumped with a $CO_2$ laser. Five new far-infrared laser lines were discovered in $^{12}CD_3OD$ and 25 in $^{13}CD_3OD$ in the range 43.697 to 719.426 μm. The frequencies of these new and some previously reported laser lines, the pump offset, the relative polarization, the relative intensity, and the optimum pressure of operation were measured.

**Key Words:** $^{12}CD_3OD$, $^{13}CD_3OD$, fully deuterated isotopomers, new laser lines, far-infrared laser, frequency measurement, $CO_2$ laser pump.

## INTRODUCTION

Thirty new far-infrared lines of methanol were discovered when optically pumping with a $CO_2$ laser: five in $^{12}CD_3OD$ and 25 in $^{13}CD_3OD$. These lie in the wavelength region from 43.697 to 719.426 μm.

Methanol and its isotopomers are the most important far-infrared (FIR) active media, generating nearly 2200 laser lines in the range 19 to 3030μm. Previous to this work, optical pumping of fully deuterated isotopomers of methanol with a $CO_2$ laser produced 214 far-infrared laser lines in $^{12}CD_3OD$ and 38 far-infrared laser lines in $^{13}CD_3OD$.[1,2] Nineteen other lines were also reported as observed when $^{12}CD_3OD$ was pumped with $CO_2$ isotope lasers.

## EXPERIMENT

A high-resolution, cw $CO_2$ laser with emission in the infrared (IR) wavelength range from 9 to 11 µm, operating on regular, hot, and sequence-band laser lines[3] was used to pump the molecules. The high-Q, Fabry-Perot laser cavity is 1.5 m long and delivers an output power of up to 40 W for the regular-band lines and up to 15 W for the sequence and hot-band lines.

The FIR laser has a 2 m long, metal-dielectric waveguide cavity and two flat end mirrors.[4] The FIR laser is longitudinally pumped with $CO_2$ radiation entering the laser through a hole in one of these end mirrors. A small, 45°, polished copper mirror near this end couples out a fraction of the FIR radiation. The other end mirror is mounted on a micrometer to tune the cavity into resonance with the FIR radiation. A Brewster-angled Si output window transmits most of the FIR, but blocks most residual $CO_2$ radiation. The FIR radiation is detected with either a pyroelectric detector or a metal-insulator-metal (MIM) diode.

## MEASUREMENTS

The $CO_2$ laser pump lines are scanned by rotating the grating and looking for absorption of the radiation by the laser media at a pressure of about 650 to 1300 Pa. Monitoring is done with the photo-acoustic signal from a microphone mounted inside the FIR laser cavity. For every pump line that shows absorption we lower and vary the pressure within a range between 40 and 800 Pa (30 and 600 mTorr). A search for FIR emission is then done by simultaneously tuning the FIR cavity length and the $CO_2$ laser pump frequency. Once a FIR laser signal is detected, the pressure, output coupling, and pump offset (the difference between the absorption frequency and the $CO_2$ laser-line-center frequency) are adjusted to optimize the signal. Then a scan of the laser modes is recorded as a function of FIR cavity length. This gives a first measurement of the number of FIR lines that lase under these conditions and their wavelengths. Finally, measuring the difference in cavity length between 20 laser modes ($10\lambda$) gives a value for the wavelength accurate to about 0.1%. This process is repeated for every $CO_2$ pump line which gives a microphone signal when absorbed by the medium.

The measured value of the wavelength is used to calculate the corresponding preliminary value of the frequency and synthesize a frequency close to this value with two locked $CO_2$ lasers. In our case the FIR radiation is mixed in a MIM diode with radiation from two reference $CO_2$ lasers and a microwave synthesizer. The diode generates frequencies of various mixing orders between these four sources. In our case

$$\delta\nu = \nu_{FIR} - n|\nu_1 - \nu_2| \pm m\nu_m, \quad (1)$$

where $\delta\nu$ is the beat frequency generated in the diode (between 0 and 1.5 GHz), $\nu_{FIR}$ is the FIR laser frequency, $\nu_1$ and $\nu_2$ are the $CO_2$ laser frequencies, and $\nu_m$ is the microwave frequency. The integers $n$ and $m$ are the mixing orders of each component. Once $\delta\nu$ is observed, the values and sign of the mixing components are determined, and the FIR laser frequency is calculated. This and other frequency measurement techniques are described in in ref. 5.

The beat frequency $\delta\nu$ from the MIM diode is amplified and observed with a spectrum analyzer.Tuning the FIR laser across its gain curve maps out the change in amplitude of $\delta\nu$ using a peak-hold feature on the spectrum analyzer.The center of this beat note is then measured with a marker frequency. Observing this beat note as the FIR and microwave radiations are changed (one at a time) gives the value and sign of $n$ and $m$. For all of these measurements $n$=1 or 2 and $m$=1 or 2. The $CO_2$ reference frequencies and the microwave frequency are chosen to give a $\delta\nu$ within the 1.5 GHz bandwidth of our amplifier and spectrum analyzer.

The $CO_2$ reference lasers are frequency-stabilized to ±10 kHz, and their frequencies are known to an accuracy of 2.5 kHz. The microwave source is also accurate within 10 Hz or less. Setting the FIR laser to the center of its gain curve determines the accuracy of the FIR laser frequency. We generally measure each frequency five times or more and report the average of these measurements. Our $1\sigma$ uncertainty is $2\times10^{-7}$ times the frequency and is due to the uncertainty in determining the center of the FIR gain curve.

Pump frequency offset measurements are important for assigning these FIR laser transitions. Measuring the offset is a simple matter of setting the pump frequency for maximum FIR power and then mixing, in a MIM diode, some of the pump radiation with a reference laser locked to the appropriate line center. Just as with the FIR frequency measurements, the diode generates a beat note between the two laser frequencies and is measured as above. Since some residual pump radiation is coupled out of the FIR laser along with the FIR radiation, any $CO_2$ filters in front of the FIR- measuring MIM diode are removed and the measurement is easily performed. For regular pump lines, the reference laser is set to the same laser transitions as the pump line. For hot and sequence- band lines, the closest regular line is used for the reference and the difference made up by a microwave synthesizer. Our pump offset measurements are reproducible to within 2 MHz. Our pump lasers free spectral range is ±37.5 MHz from line center, so any offset measurements ≥38 MHz are very near the edge of the $CO_2$ gain curve.

The polarization of each FIR laser line relative to the polarization of the pump laser, the relative intensity of each FIR laser line, and its optimum pressure were also recorded.

## RESULTS AND COMMENTS

In Table 1 the 30 new and the two previously known FIR laser lines observed in the fully deuterated methanol, along with their pump line, relative intensity, relative polarization, pressure, and frequency offsets of the pump laser are reported. The new lines have wavelengths in the range 43.697 to 719.426 μm. Most of them are of medium and strong relative intensity.The 10R(18) pumped 43.697 μm line is the strongest. The line 62.6 μm in $^{13}CD_3OD$, pumped by 10R(8)′, is rated as weak, and coincidentally there is a 63.0 μm line in $^{13}CD_3OH$ also pumped by 10R(8), reported as having medium relative intensity.[8] Frequency measurements of both lines are not available yet. Once measured they will allow us to determine if they refer to the same line. If they are the same line then the line appearing weaker in the fully deuterated methanol is probably due to contamination caused by the exchange of OH for OD on the walls of the laser.

In Table 2 the lines are presented in order of increasing wavelength, with their frequency measurements, their calculated wavelengths, and calculated wavenumbers (calculated from their measured frequencies using c = 299 792 458 m/s) also included. The frequencies are in the range 416 710.4 to 6 860 664.6 MHz .

Previous reports have shown only 33 frequency measured lines for the fully deuterated isotopomers of methanol. Our work adds 28 new frequency measured lines, and there are still many more frequencies to be measured. Sixteen percent of these lines have wavelengths shorter than 100 µm and these are the ones needed for applications in the spectroscopy of free radicals and ions where there is a shortage of lines.

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Table 1. Far-infrared laser lines from optically pumped $^{12}CD_3OD$ and $^{13}CD_3OD$

| $CO_2$ Pump Laser | Wavelength µm | Offset MHz | Pressure Pa(mTorr) | Pol. | Rel. Int. | Ref. |
|---|---|---|---|---|---|---|
| $^{12}CD_3OD$ | | | | | | |
| 9R(50)' | 246.2 | | 27(200) | // | S | new |
| 10R(52) | 265.019 | | 15(110) | // | W | new |
| 10R(48)' | 45.362 | | 27(200) | // | M | new |
| 10R(48)" | 79.257 | | 11(80) | // | W | new |
| 10R(34) | 180.741 | | 52(390) | ⊥ | W | 3 |
| 10R(18) | 43.697 | | 21(160) | ⊥ | VS | new |

| $CO_2$ Pump Laser | Wavelength μm | Offset MHz | Pressure Pa(mTorr) | Pol. | Rel. Int. | Ref. |
|---|---|---|---|---|---|---|
| **$^{13}CD_3OD$** | | | | | | |
| 10R(54) | 215.005 | +22 | 19(140) | // | M | new |
| 10R(52) | 105.696 | +26 | 43(320) | // | M | new |
| 10R(50) | 132.862 | -19 | 23(170) | ⊥ | M | new |
| 10R(46) | 52.2 | | 27(200) | // | W | new |
| 10R(44) | 65.449 | -44 | 55(410) | // | S | new |
| | 134.920 | +3 | 13(100) | // | W | new |
| | 140.354 | | 28(210) | // | M | new |
| 10R(40)′ | 70.947 | | 33(250) | // | M | new |
| 10R(40)″ | 164.142 | -32 | 21(160) | // | S | new |
| 10R(38) | 719.426 | 0 | 20(150) | // | M | new |
| 10R(32)′ | 46.4 | | 16(120) | // | W | new |
| 10R(32)″ | 72.194 | +17 | 16(120) | // | M | new |
| 10R(28) | 252.738 | +6. | 11(80) | // | M | new |
| 10R(26) | 146.326 | -28 | 24(180) | ⊥ | S | new |
| 10R(24) | 90.155 | | 35(260) | // | M | new |
| 10SR(23) | 54.159 | | 17(130) | // | W | new |
| 10SR(17)′ | 95.93 | -18 | 24(180) | ⊥ | M | new |
| 10SR(17)″ | 100.506 | -21 | 23(170) | // | M | new |
| 10SR(17)′″ | 110.6 | | 23(170) | // | W | new |
| 10R(12) | 215.466 | +37 | 29(220) | // | W | new |
| 10SR(13) | 74.817 | | 21(160) | // | W | new |

| $CO_2$ Pump Laser | Wavelength μm | Offset MHz | Pressure Pa(mTorr) | Pol. | Rel. Int. | Ref. |
|---|---|---|---|---|---|---|
| 10R(8)′ | 62.6 | | 33(250) | // | W | new |
| 10R(8)″ | 464.455 | -9 | 13(100) | // | S | 4 |
| 10R(4) | 138.040 | +3 | 20(150) | // | W | new |
| 10R(2) | 298.811 | +28 | 20(150) | // | M | new |
| 10P(8) | 146.129 | | 16(120) | // | M | new |

′, ″, and ‴ indicate different $CO_2$ laser frequency offsets.

able 2. List of laser lines of $^{12}CD_3OD$ and $^{13}CD_3OD$ by increasing wavelength and frequency measurements.

| $CO_2$ Laser | Frequency[a] MHz | Wavelength[b] μm | Wavenumber[b] $cm^{-1}$ | Pressure Pa(mTorr) | Rel. Int. | Offset MHz |
|---|---|---|---|---|---|---|
| **$^{12}CD_3OD$** | | | | | | |
| 10R(18) | 6 860 664.6 | 43.697 | 228.8471 | 21(160) | VS | |
| 10R(48)′ | 6 608 862.5 | 45.362 | 220.4479 | 27(200) | M | |
| 10R(48)″ | 3 782 558.7 | 79.257 | 126.1726 | 11(80) | W | |
| 10R(34) | 1 658 687.9 | 180.741[c] | 55.3279 | 52(390) | W | |
| 9R(50) | | 246.2 | 40.62 | 27(200) | S | |
| 10R(52) | 1 131 211.7 | 265.019 | 37.7332 | 15(110) | W | |
| **$^{13}CD_3OD$** | | | | | | |
| 10R(32)′ | | 46.4 | 215.52 | 16(120) | W | |
| 10R(46) | | 52.2 | 191.57 | 27(200) | W | |
| 10SR(23) | 5 535 464.2 | 54.159 | 184.6432 | 17(130) | W | |

| $CO_2$ Laser | Frequency[a] MHz | Wavelength[b] μm | Wavenumber[b] $cm^{-1}$ | Pressure Pa(mTorr) | Rel. Int. | Offset MHz | Rel. Pol. |
|---|---|---|---|---|---|---|---|
| 10R(8)′ | | 62.6[c] | 159.74 | 33(250) | W | | // |
| 10R(44) | 4 580 534.6 | 65.449 | 152.7902 | 55(410) | S | -44 | // |
| 10R(40) | 4 225 588.4 | 70.947 | 140.9505 | 33(250) | M | | // |
| 10R(32)″ | 4 152 617.0 | 72.194 | 138.5164 | 16(120) | M | 17 | // |
| 10SR(13) | 4 007 023.0 | 74.817 | 133.6599 | 21(160) | W | | // |
| 10R(24) | 3 325 304.5 | 90.155[c] | 110.9202 | 35(260) | M | | // |
| 10SR(17)′ | 3 125 109.1 | 95.93 | 104.2424 | 24(180) | M | -18 | ⊥ |
| 10SR(17)″ | 2 982 828.9 | 100.506 | 99.4965 | 23(170) | M | -21 | // |
| 10R(52) | 2 836 366.0 | 105.696 | 94.611 | 43(320) | M | 26 | // |
| 10SR(17)′″ | | 110.6 | 90.42 | 23(170) | W | | // |
| 10R(50) | 2 256 426.6 | 132.862 | 75.2663 | 23(170) | M | -19 | ⊥ |
| 10R(44) | 2 222 002.5 | 134.92 | 74.118 | 13(100) | W | 3 | // |
| 10R(4) | 2 171 779.5 | 138.04 | 72.4428 | 20(150) | W | 3 | // |
| 10R(44) | 2 135 979.8 | 140.354 | 71.2486 | 28(210) | M | | // |
| 10P(8) | 2 051 564.5 | 146.129 | 68.4328 | 16(120) | M | | // |
| 10R(26) | 2 048 803.8 | 146.326[c] | 68.3407 | 24(180) | S | -28 | ⊥ |
| 10R(40) | 1 826 416.2 | 164.142 | 60.9227 | 21(160) | S | -32 | // |
| 10R(54) | 1 394 348.0 | 215.005 | 46.5104 | 19(140) | M | 22 | // |
| 10R(12) | 1 391 365.1 | 215.466 | 46.4109 | 29(220) | W | 37 | // |
| 10R(28) | 1 186 180.4 | 252.738 | 39.5667 | 11(80) | M | 6 | // |
| 10R(2) | 1 003 282.9 | 298.811 | 33.4659 | 20(150) | M | 28 | // |
| 10R(8)″ | 645 471.7 | 464.455[c] | 21.5306 | 13(100) | S | -9 | // |
| 10R(38) | 416 710.4 | 719.426 | 13.9 | 20(150) | M | 0 | // |

[a] estir
[b] calc
[c] not

′, ″ and ‴ indicate different $CO_2$ laser frequency offsets.
[a] estimated uncertainty in the reproducibility of the FIR laser frequency: $\Delta\nu/\nu = 2 \times 10^{-7}$.
[b] calculated from the measured frequency with c= 299 792 458 m/s.
[c] not a new line, see reference in Table 1.

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