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New laser lines from CHD₂OH methanol deuterated isotope

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ABSTRACT Through the optical pump technique we have reinvestigated the CHD₂OH molecule as a source of far-infrared (FIR) laser lines using for the first time a CO₂ laser lasing on regular, hot, and sequence bands. As a consequence, we present here spectroscopic data of 16 new FIR laser transitions from this molecule. Furthermore, we also present a catalogue of all FIR laser lines generated from CHD₂OH.

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1 Introduction

Methanol is the most important lasing molecule in the far-infrared (FIR) spectra, and the most widely used for investigations and applications. The main reason for its success as a laser source is the excellent overlap of the strong absorbing C–O stretch mode of this molecule with the CO₂ laser lines that are the most used as pump sources. The substitution of H by D, ¹²C by ¹³C, or ¹⁶O by ¹⁸O in the molecule does not appreciably shift this absorption. As a consequence, methanol and its isotopes together have been recognized as efficient sources for generation of FIR laser lines [1–3]. Particularly, the CHD₂OH deuterated isotope has been little investigated up to now. FIR laser action optically pumped from this molecule was first reported by Ziegler and Dürr [4] in 1978 and subsequently by Facin et al. [5] in 1989. The total number of FIR lines reported was 93. For this reason we have undertaken an experimental study of this molecule in order to find new laser lines, using for the first time a CO₂ laser that lases on regular, hot, and sequence bands.

In this work we report 16 new FIR laser lines from CHD₂OH, ranging from 34.2 to 192 μm. Data relative to each line are very important for spectroscopic investigations and applications, and therefore we present here a complete catalogue of all the FIR laser lines of this molecule including the lines observed by us.

2 Experimental results

The experimental apparatus consists of a 2-m-long cw CO₂ pump laser and a versatile Fabry–Perot FIR laser cavity. The CO₂ laser has a grating specially blazed to provide approximately 3% output coupling in the zeroth order from 9 to 11 μm. A total of 230 CO₂ laser lines from sequence, hot, and regular bands were available. A detailed description of this laser can be obtained from [6, 7].

The FIR laser cavity is formed by two gold-coated copper concave mirrors with a radius of curvature of 1.9 m and separated by ~ 2 m. One mirror is fixed, while the other is moveable and coupled to a micrometer allowing tuning of the cavity into resonance with the longitudinal modes of the FIR laser. A variable resistor biased at 1.5 VDC (output range 0 to 1.5 VDC) is coupled to the micrometer to provide an output in the *x* direction to an *x*–*y* plotter. For each wavelength measurement the cavity was scanned over several longitudinal modes, and the intensity was plotted as a function of cavity length. This allowed us to determine the FIR laser wavelengths with an uncertainty of approximately ±0.5 μm. The FIR output power is coupled by a 45° mirror (radially adjustable) and was detected using a pyroelectric detector. We have used the cavity in a V-type configuration [8, 9] to perform this work.

The source gas used in this experiment had an isotopic purity of 98% at minimum. To ensure that the observed laser lines were actually of CHD₂OH we kept a little gas flow in the FIR cavity.

3 Results and comments

All of the lines observed up to now, including this work, are listed in Table 1 sorted by CO₂ pump line, with a reference to the authors who first observed the line. For the 16 new lines observed by us we give the wavelength, the polarization relative to that of the pumping CO₂ laser, the optimum pressure of operation, and the relative intensity. The intensity of each line was measured and calibrated against the intensity of the 118.8-μm line from ¹²CH₃OH [8]. For the lines known before this work, we keep the intensity notation used by the authors. Ziegler et al. [4] used strong (S), medium (M), and weak (W) to denote the line intensity, considering as strong

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| Pump line | Laser line (μm) | Laser line (cm^{-1}) | Rel. pol. | Press. (Pa) | Rel. int. | CO ₂ power (W) | Ref. | Pump line | Laser line (μm) | Laser line (cm^{-1}) | Rel. pol. | Press. (Pa) | Rel. int. | CO ₂ power (W) | Ref. |
|-----------|------------------------------|---------------------------------|-----------|-------------|-----------|---------------------------|------|-----------|------------------------------|---------------------------------|-----------|-------------|-----------|---------------------------|------|
| 9R50 | 54.8 | 182.48 | ⊥ | 21 | 0.5 | | New | 10R20 | 172.1 | 58.11 | | 24 | 4 | 18 | 5 |
| 9R38 | 109.3 | 91.49 | ⊥ | 19 | 12.9 | 8.5 | 5 | | 260 | 38.46 | | 11 | S | | 4 |
| | 111.4 | 89.77 | ⊥ | 19 | 6.4 | 8.5 | 5 | 10R18 | 55.6 | 179.86 | | 15 | 20.1 | 18 | 5 |
| | 117.3 | 85.25 | ⊥ | 19 | 8.5 | 8.5 | 5 | | 127.4 | 78.49 | | 21 | 22.4 | 17 | 5 |
| | 172.4 | 58.00 | | 16 | 1.3 | 8.5 | 5 | | 259.9 | 38.48 | | 21 | 7.7 | 15 | 5 |
| 9R34 | 279.0 | 35.84 | | 9 | 0.3 | 12 | 5 | 10R16 | 55.8 | 179.21 | | 16 | 0.6 | | New |
| | 290.2 | 34.46 | | 9 | 0.4 | 12 | 5 | | 179 | 55.87 | | 11 | M | | 4 |
| 9R32 | 145.3 | 68.82 | ⊥ | 15 | 5.4 | 14 | 5 | | 363 | 27.55 | | 11 | S | | 4* |
| | 179.8 | 55.62 | | 16 | 5.2 | 14 | 5 | 10R14 | 83.7 | 119.47 | ⊥ | 25 | 3.7 | 17 | 5 |
| 9R30 | 120.9 | 92.71 | | 24 | 12.1 | 15 | 5 | 10R10 | 228.7 | 43.73 | | 16 | 10.7 | 17 | 5 |
| | 132.2 | 75.64 | ⊥ | 13 | 3 | 15 | 5 | | 270.0 | 37.04 | | 13 | 0.5 | 17 | 5 |
| 9R26 | 135.0 | 74.07 | ⊥ | 15 | 1.2 | 15 | 5 | 10R08 | 305.6 | 32.72 | | 16 | 27.8 | 15 | 5 |
| | 144.8 | 69.06 | ⊥ | 15 | 0.6 | 15 | 5 | | 452.5 | 22.10 | | 21 | 33.1 | 17.5 | 5 |
| | 202.6 | 49.36 | | 15 | 3 | 15 | 5 | 10R06 | 105.0 | 95.24 | | 27 | 2.8 | 16 | 5 |
| 9R24 | 164.4 | 60.83 | | 12 | 4.8 | 15 | 5 | 10R04 | 74.1 | 134.95 | | 16 | 0.3 | 12 | 5 |
| 9R20 | 249.6 | 40.06 | | 11 | 0.7 | 17 | 5 | 10R02 | 344.9 | 28.99 | | 11 | 0.9 | 8 | 5 |
| 9R18 | 140.7 | 71.07 | | 27 | 3 | | New | 10P04 | 57.9 | 172.71 | ⊥ | 15 | 4.5 | 13 | 5 |
| | 165 | 60.61 | | 11 | M | | 4* | 10P08 | 123.8 | 80.78 | | 12 | 19.3 | 15 | 5 |
| 9R16 | 217.9 | 45.89 | | 21 | 52.1 | 16 | 5 | | 152.6 | 65.53 | ⊥ | 15 | 30.2 | 15 | 5 |
| 9R14 | 280.8 | 35.61 | | 19 | 18.1 | 15 | 5 | 10P10 | 517.8 | 19.31 | | 12 | 1.2 | 16.5 | 5 |
| | 317.0 | 31.55 | | 16 | 36.2 | 16 | 5 | 10P12 | 171.1 | 58.45 | | 13 | 42.7 | 17 | 5 |
| | 598.3 | 16.71 | | 16 | 11.3 | 16 | 5 | 10P14 | 103.0 | 97.09 | ⊥ | 25 | 66.1 | 17 | 5 |
| 9R10 | 221.2 | 45.21 | | 19 | 0.4 | 13 | 5 | 10P16 | 103.0 | 97.09 | | 27 | 85.3 | 17 | 5 |
| 9R04 | 45.6 | 219.30 | ⊥ | 25 | 2.7 | | New | 10P18 | 46.8 | 213.68 | | 17 | 0.3 | | New |
| | 78.2 | 127.88 | | 27 | 2.7 | | New | | 174.9 | 57.18 | ⊥ | 27 | 0.1 | | New |
| | 165.1 | 60.57 | | 15 | 21.1 | 12 | 5 | | 238 | 42.02 | | 11 | S | | 4* |
| 9P04 | 246.8 | 40.52 | | 15 | 34 | 8 | 5 | | 355 | 28.17 | | 11 | M | | 4 |
| | 512.8 | 19.50 | | 16 | 11.3 | 8 | 5 | | 212.9 | 46.97 | ⊥ | 21 | 102 | 17 | 5 |
| 9P06 | 34.2 | 292.40 | | 12 | 2.3 | | New | 10P20 | 291.3 | 34.33 | | 15 | 45.3 | 18 | 5 |
| | 483 | 20.70 | | 11,15 | W,24.9 | 8 | 4,5 | | 427.1 | 23.41 | | 15 | 40.3 | 18 | 5 |
| 9P08 | 196.8 | 50.81 | | 16 | 6 | 9 | 5 | 10P28 | 74.8 | 133.69 | ⊥ | 15 | 1.2 | 18 | 5 |
| 9P16 | 226.8 | 44.09 | | 16 | 2 | 10 | 5 | | 124.4 | 80.39 | ⊥ | 15 | 6 | 18 | 5 |
| 9P18 | 104.6 | 95.60 | | 16 | 9.9 | 11 | 5 | | 558.8 | 17.90 | ⊥ | 16 | 10.1 | 18 | 5 |
| | 165.1 | 74.02 | | 8 | 0.1 | | New | 10P40 | 125.4 | 79.74 | | 16 | 2.7 | 10 | 5 |
| 9P20 | 346 | 28.90 | | 11 | W | | 4 | | 142.9 | 69.98 | ⊥ | 16 | 2.7 | 10 | 5 |
| | 246.1 | 40.63 | | 15 | 1.4 | 10 | 5 | 10SR11 | 53.3 | 187.62 | | 7 | 0.2 | | New |
| | 254.3 | 39.35 | | 13 | 90.6 | 12 | 5 | 10SP11 | 128.2 | 78.00 | | 10 | 0.1 | | New |
| | 501.9 | 19.92 | | 13 | 0.9 | 10 | 5 | 10HP16 | 143.4 | 69.74 | | 20 | 0.3 | | New |
| 9P22 | 484.4 | 20.64 | | 13 | 1.5 | 12 | 5 | | 150.7 | 66.36 | | 20 | 0.1 | | New |
| 9P24 | 203.1 | 49.24 | | 24 | 6.6 | 12 | 5 | | | | | | | | |
| 9P26 | 128.5 | 77.82 | ⊥ | 16 | 5.6 | 13 | 5 | | | | | | | | |
| | 204.7 | 48.85 | | 21 | 3.8 | 14.5 | 5 | | | | | | | | |
| | 255.3 | 39.17 | ⊥ | 9 | 1.7 | 13 | 5 | | | | | | | | |
| | 437.4 | 22.86 | | 11 | 2.5 | 10 | 5 | | | | | | | | |
| 9P28 | 404.6 | 24.72 | | 11 | 10.5 | 10 | 5 | | | | | | | | |
| 9P30 | 518 | 19.31 | | 11 | M | | 4 | | | | | | | | |
| | 385.4 | 25.95 | | 13 | 63.4 | 10 | 5 | | | | | | | | |
| 9P34 | 137.0 | 72.99 | | 11 | 9.1 | 10 | 5 | | | | | | | | |
| | 606.7 | 16.48 | ⊥ | 13 | 6.3 | 10 | 5 | | | | | | | | |
| | 607.3 | 16.47 | | 11 | 5.1 | 10 | 5 | | | | | | | | |
| 9P36 | 249.7 | 40.05 | | 15 | 1.7 | 11 | 5 | | | | | | | | |
| 9P38 | 123.9 | 80.71 | ⊥ | 16 | 19.9 | 10 | 5 | | | | | | | | |
| | 187.5 | 53.33 | | 15 | 6.6 | 11 | 5 | | | | | | | | |
| 9P50 | 60.5 | 165.29 | ⊥ | 20 | 0.5 | | New | | | | | | | | |
| | 158.5 | 63.09 | ⊥ | 17 | 0.1 | | New | | | | | | | | |
| | 192.0 | 52.08 | | 17 | 0.3 | | New | | | | | | | | |
| 10R40 | 111.6 | 89.61 | | 8 | 16.1 | 9 | 5 | | | | | | | | |
| | 80.0 | 125.00 | ⊥ | 16 | 3.6 | 10 | 5 | | | | | | | | |
| 10R38 | 168 | 59.52 | | 11 | M | | 4 | | | | | | | | |
| | 426 | 23.47 | | 11 | M | | 4 | | | | | | | | |
| 10R36 | 278.4 | 35.92 | | 21 | 2.8 | 13 | 5 | | | | | | | | |
| 10R34 | 111.9 | 89.37 | | 16 | 9 | 12 | 5 | | | | | | | | |
| 10R32 | 83.9 | 119.19 | ⊥ | 11 | 1.3 | 14 | 5 | | | | | | | | |
| | 93.0 | 107.53 | | 15 | 2.5 | 14.5 | 5 | | | | | | | | |
| 10R28 | 227.5 | 43.96 | | 15 | 1.1 | 17 | 5 | | | | | | | | |
| 10R26 | 41.8 | 239.23 | ⊥ | 11 | 0.5 | 11 | 5 | | | | | | | | |
| | 45.1 | 221.73 | | 11 | 1.8 | 11 | 5 | | | | | | | | |
| | 136.2 | 73.42 | | 12 | 4.2 | 13 | 5 | | | | | | | | |
| 10R24 | 107.4 | 93.1 | | 19 | 0.6 | 12.5 | 5 | | | | | | | | |
| 10R22 | 288.3 | 25.75 | | 19 | 2.5 | 11 | 5 | | | | | | | | |

* Lines also observed from CH₂DOH by the same author. S. Kon et al. in [1] (p. 169) observed that these lines may be from CHD₂OH

More information:

Ziegler and Dürr [4]: cw CO₂ laser; wavelengths were measured to an accuracy of $\pm 0.5 \text{ cm}^{-1}$

Facin et al. [5]: cw CO₂ laser with 75 MHz of tuning; the intensity was normalized with respect to the 118.8-cm^{-1} line of ¹²CH₃OH oscillating in the same cavity

TABLE 1 FIR laser lines from CHD₂OH

that line that provides a power of approximately 1–2 mW, and as weak that line with a power of about 0.5 mW or less. All the lines reported by Facin et al. [5] had their intensities normalized with respect to the intensity of the $118.8\text{-}\mu\text{m}$ line of ¹²CH₃OH oscillating in the same cavity. Other important information about the FIR and CO₂ laser lines is presented at the end of Table 1.

All the 16 new lines reported here have a wavelength smaller than 200 μm , due to the Fabry–Perot laser cavity having a diffractive loss less than 0.5% at wavelengths below 150 μm . In Table 2 we compare the wavelength spectrum repartition of the FIR lines obtained by us and by other authors. The number of laser lines observed by us with a wavelength below 150 μm represents an increase of 32% with respect to the total observed before this work. Moreover, we can also observe that most FIR laser lines from CHD₂OH present

| Reference | FIR line number | Lines < 150 μm | Lines 150–300 μm | Lines > 300 μm |
|-------------|-----------------|----------------|------------------|----------------|
| 4 | 11 | | 5 | 6 |
| 5 | 82 | 34 | 32 | 16 |
| Our results | 16 | 11 | 5 | |
| Total | 109 | 45 | 42 | 22 |

TABLE 2 Wavelength spectral repartition of FIR laser lines from CHD₂OH

a short wavelength. From 109 lines, 87 of them have wavelengths smaller than 300 μm.

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