*International Journal of Infrared and Millimeter Waves, Vol. 12, No. 10, 1991*

# FAR INFRARED LASER FREQUENCIES OF $CH_3OD$ AND $N_2H_4$

**H. E. Radford,[1] K. M. Evenson,[2] F. Matushima,[2,4] L. R. Zink,[2] G. P. Galvao,[2,5] and T. J. Sears[3]**

[1]*Atomic and Molecular Physics Division*
*Harvard-Smithsonian Center for Astrophysics*
*Cambridge, Massachusetts 02138*

[2]*Time and Frequency Division*
*National Institute of Standards and Technology*
*Boulder, Colorado 80303*

[3]*Department of Chemistry*
*Brookhaven National Laboratory*
*Upton, New York, 11973*

Received July 10, 1991

[4] Permanent address: Dept. of Physics, Toyama University, Gofuku 3190, Toyama 930, Japan.

[5] Permanent address: Instituto Nacional de Pesquisas Espaciais, 12.201 - Sao José dos Campos, SP, Brazil.





0195-9271/91/1000-1161$06.50/0 © 1991 Plenum Publishing Corporation

## Abstract

The frequencies of 26 laser lines with wavelengths between 57 and 534 μm have been measured in the optically pumped laser gases $CH_3OD$ and $N_2H_4$. A pair of stabilized cw $^{12}CO_2$ lasers was used as a frequency standard for the heterodyne frequency measurements. Seven of the 26 lines are new.


Key words: $CH_3OD$, $N_2H_4$, molecular laser lines, laser frequency measurements, optically pumped far infrared lasers.

## Introduction

Methanol-OD ($CH_3OD$) and hydrazine ($N_2H_4$) contribute at least 173 lines to the list of known far infrared (FIR) laser lines[1], but accurate measurements of line frequencies have been made for only a few of them[2]. This came forcefully to our attention after we had observed and tried to analyze some new laser magnetic resonance (LMR) spectra, and found that some of the best of these were produced by laser lines of methanol-OD and hydrazine for which no accurate frequencies were known. While remedying this situation for the few lines that were of direct interest to us, we have gone on to measure frequencies for a number of other lines of these two laser molecules that had escaped attention in the past and that operate readily in our transversely-pumped cw laser. This type of laser, a favorite for far infrared LMR spectroscopy, is also well suited to precise frequency measurements because of its decoupling of the pump laser from the far infrared resonator[3]. With careful adjustment of a transversely-pumped resonator to the top of a symmetrical gain curve, relative frequency repeatabilities of $\pm 2 \times 10^{-7}$ can be achieved[4]. This is adequate for the analysis of LMR spectra in which errors in magnetic field measurements are often much larger.

Because our measurements are oriented toward spectroscopic applications of far infrared lasers where broad, dense, frequency coverage is essential, we have been careful to investigate every strong pump absorption of the two molecules for new lines that might be made to lase by varying the laser gas pressure and the tuning of the pump laser. We have not measured the polarizations or output powers of the laser lines.

## Measurements

The experimental technique is that developed in this laboratory over the past several years and applied chiefly to the other isotopic variants of methanol[2,4,5]. The laser gas fills a copper tube, 5 cm in diameter, located between the mirrors of a near-confocal Fabry-Perot resonator 1 m long. Pump radiation from a cw $^{12}CO_2$ laser, of 40 w maximum power output, enters the tube near one end, through a window in the side wall at an angle of 75° with respect to the axis. The far infrared output is taken off a polypropylene intracavity membrane, 12.5 μm thick, variable in angle about the Brewster angle. A co-rotating mirror keeps the output beam fixed in direction. This is a change over the previous practice of taking output from a small mirror located in the outer region of the laser mode and provides better focussing onto the detector, a long-wire W-Ni point contact diode. Also focussed onto the diode are the output beams of the two stabilized $CO_2$ reference lasers, each tuned to a different line of $CO_2$. Provision is also made to capacitively couple radiation from a synthesized microwave generator to the diode with a 1 cm extension of the center conductor of a coaxial cable. These three reference frequencies are chosen to generate a beat frequency with the far infrared laser through the non-linear properties of the diode. The beat frequency is within the 0 - 1.5 GHz range of a commercial spectrum analyzer. The approximate far infrared laser frequencies are obtained by scanning the movable Fabry-Perot mirror over a large number of axial modes of the laser oscillation. The beat frequency is amplified and displayed on the spectrum analyzer using a peak hold feature that records the shape of the gain curve of the far infrared laser as it is tuned. The peak frequency of the gain curve is measured with a marker oscillator and frequency counter.

## Results and Discussion

The results of the frequency measurements are collected in Table 1 for methanol-OD and Table 2 for hydrazine. For both laser gases the spectral distribution of lines is largest in the 100-300 μm region, thus helping to fill the voids in the distribution of measured lines given by reference 2. Three of the 26 newly measured lines lie shorter than 100 μm, a very sparsely populated region for optically pumped lasers.

Table 1. Summary of $CH_3OD$ laser line frequency measurements

| Wavelength (μm) | Frequency[a] (MHz) | Pressure[b] Pa(mTorr) | Pump Line[c] ($^{12}CO_2$) | Notes |
|---|---|---|---|---|
| 57.1 | 5 245 612.9 | 13(100) | 9R(8) | d |
| 81.7 | 3 669 048.5 | 20(150) | 9P(30)‴ | e |
| 110.1 | 2 726 037.6 | 16(120) | 10R(44) | |
| 144.8 | 2 070 440.5 | 15(110) | 9P(32) | New |
| 151.8 | 1 974 905.8 | 10(75) | 9R(2) | New |
| 167.5 | 1 789 767.5 | 7(50) | 9P(30)″ | |
| 176.1 | 1 702 843.4 | 9(70) | 9R(2) | New |
| 212.7 | 1 409 666.3 | 8(60) | 9R(6)‴ | New |
| 220.3 | 1 360 677.6 | 10(75) | 9R(6)′ | |
| 230.6 | 1 299 994.8 | | 9P(6) | |
| 239.8 | 1 249 966.3 | 13(100) | 10R(44) | |
| 292.6 | 1 024 510.0 | 13(100) | 9R(6)″ | New |
| 332.1 | 902 630.2 | | 9R(4) | |
| 352.5 | 850 412.0 | 16(120) | 9P(30)″ | |
| 418.2 | 716 947.3 | 21(160) | 9P(6) | |
| 515.1 | 582 026.4 | 13(100) | 9P(6) | |

a. Unless otherwise noted, the estimated relative frequency uncertainty is $\pm 2 \times 10^{-7}$.
b. Measured with a thermocouple gauge calibrated for air (1 Torr □ 133.3 Pa).
c. Multiple absorptions by the far infrared laser gas within the piezoelectric tuning range of the pump laser are indicated by prime marks. For the 9P(30) line there are three absorptions, with 9P(30)′ yielding the previously measured 103.1 μm line.
d. Estimated error is ±1.5 MHz due to asymmetric gain curve.
e. This pump frequency also produces 145.7 μm.

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The discovery of seven new cw laser lines in these two well-known laser gases, using only moderate pump power and gain length, suggests that re-searching other known far infrared laser gases might be similarly productive. The essential point is that within the range over which the $CO_2$ pump laser frequency can be pulled by cavity length tuning, typically 100 MHz for a 1.5 m laser, there may be several IR absorptions by the laser gas that are capable of generating FIR laser emission. In general, each will have its own optimum gas pressure. The common practice of accepting and optimizing the first laser line that is found with a given pump line discriminates against the other possible lines, and can cause them to be missed. The case of methanol-OD pumped by 9P(30) is a good example: here are five easily produced cw laser lines (two, previously measured, are not included in Table 1), each with a different optimum pressure and with three different piezoelectric tuning offsets.

Table 2. Summary of $N_2H_4$ laser line frequency measurements

| Wavelength (μm) | Frequency[a] (MHz) | Pressure[b] Pa(mTorr) | Pump Line[c] ($^{12}CO_2$) | Notes |
|---|---|---|---|---|
| 81.2 | 3 690 723.1 | 40(300) | 10P(16)'' | |
| 102.6 | 2 923 359.0 | 27(200) | 10P(16)'' | |
| 134.9 | 2 221 963.2 | 27(200) | 10P(6)' | |
| 137.9 | 2 174 579.3 | 27(200) | 10P(6)'' | New |
| 143.2 | 2 092 854.4 | 13(100) | 10R(20) | |
| 150.7 | 1 989 217.5 | | 10R(4) | New |
| 235.6 | 1 272 681.1 | 20(150) | 10R(38) | |
| 373.6 | 802 492.8 | 20(150) | 10R(12) | |
| 533.7 | 561 771.3 | 13(100) | 10R(8) | |
| 533.7 | 561 773.0 | 13(100) | 10R(8) | d |

a. Unless otherwise noted, the estimated relative frequency uncertainty is $\pm 2 \times 10^{-7}$.
b. Measured with a thermocouple guage calibrated for air (1 Torr = 133.3 Pa).
c. Multiple absorptions by the far infrared laser gas within the piezoelectric tuning range of the pump laser are indicated by prime marks. For the 10P(16) line there are two absorptions, with 10P(16)' yielding the previously measured 461.1 μm line.
d. This is the weaker line of the pair.

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The 533.7 μm line of hydrazine has been known to be a renegade for some time. LMR spectra observed with this line appear and disappear mysteriously, and its absorption by foreign gases is erratic. Formic acid vapor in particular sometimes absorbs this line so strongly as to put out the laser, but at other times does not absorb it at all. The reason for this behavior is revealed by the frequency measurement of the line: it consists of two very close components. They are separated by only 1.74 MHz, the higher frequency line being the weaker by a factor of 2 (this is the component that is absorbed by formic acid). Depending on the operating conditions of the far infrared laser, either or both of these lines may oscillate.

## Acknowledgements

This work was supported in part by NASA GRANT W-15, 047. Work at Brookhaven National Laboratory was carried out under contract number DE-AC02-76CH00016 with the United States Department of Energy and supported by its Division of Chemical Sciences, Office of Basic Energy Sciences.

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