Reinvestigation of Far-Infrared Laser Emissions From Hydrazine and Deuterated Isotopes of Difluoromethane and Methanol

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ABSTRACT

Hydrazine (N_2H_4) and deuterated isotopes of difluoromethane (CD_2F_2) and methanol (CH_3OD, CH_2DOH and CD_3OH) have been reinvestigated as sources of far-infrared (FIR) laser emissions using an optically pumped molecular laser system designed for wavelengths below 150 micron. With this system, eleven FIR laser emissions from optically pumped N_2H_4, CH_3OD, CH_2DOH, and CD_3OH were discovered with wavelengths ranging from 49 to 185 μm. In addition, the polarizations of eight previously observed laser emissions from optically pumped N_2H_4, CH_3OD and CD_2F_2 were measured for the first time. All laser emissions are reported with their operating pressure, relative polarizations and wavelengths, measured to ± 0.5 μm. The effectiveness of this particular system in generating short-wavelength laser emissions has been further demonstrated by the improvement in output power observed from nine known FIR laser emissions.

INTRODUCTION

A significantly improved optically pumped molecular laser (OPML) system was recently developed to generate short-wavelength (below 150 μm) laser emissions in the far-infrared [1]. Prior to the present work, forty laser emissions have been discovered with this system from several optically pumped methanol isotopes (CD_3OH, CHD_2OH, $^{13}CD_3OD$, and $^{13}CH_3OH$) ranging in wavelength from 26.3 to 174.6 μm [1-4]. The objective of this work was to further investigate the effectiveness of this OPML system in the discovery of short-wavelength FIR laser emissions.

Several molecules were selected for reinvestigation with this experimental system, either because they have produced many short-wavelength laser lines or because they have not been studied in a FIR laser cavity designed for short-wavelength emissions. These molecules are N_2H_4, N_2D_4, CD_2F_2, CH_3OD, CH_2DOH and CD_3OH. Hydrazine, N_2H_4, is an extremely rich and efficient laser-active medium capable of providing over 230 FIR laser emissions, about 35% of which are below 150 μm. This molecule has been the subject of several recent theoretical and experimental investigations [5-8], including a comprehensive review [9]. Unlike its parent species, the fully deuterated isotope of hydrazine, N_2D_4, has gone fairly unnoticed and was the subject of only one investigation that resulted in the generation of 31 laser emissions in the FIR region [10]. Similarly, deuterated difluoromethane, CD_2F_2 has not been studied extensively [11-13] and has been reported to contribute 57 FIR laser emissions. The partially deuterated isotope of methanol, CH_3OD, which has been the subject of several recent studies [14-16], was also selected for reinvestigation. CH_3OD has been found to produce over 180 laser emissions in the far-infrared [14-18], with about 45% having wavelengths shorter than 150 μm. CH_2DOH has also been the subject of several studies, resulting in the discovery of over 140 laser emissions [14, 19-21]. This isotope was selected for reinvestigation because of the number of laser emissions it has been known to generate below 150 micron (over 25%). Finally CD_3OH, which was previously studied with this system [1], was also reinvestigated.

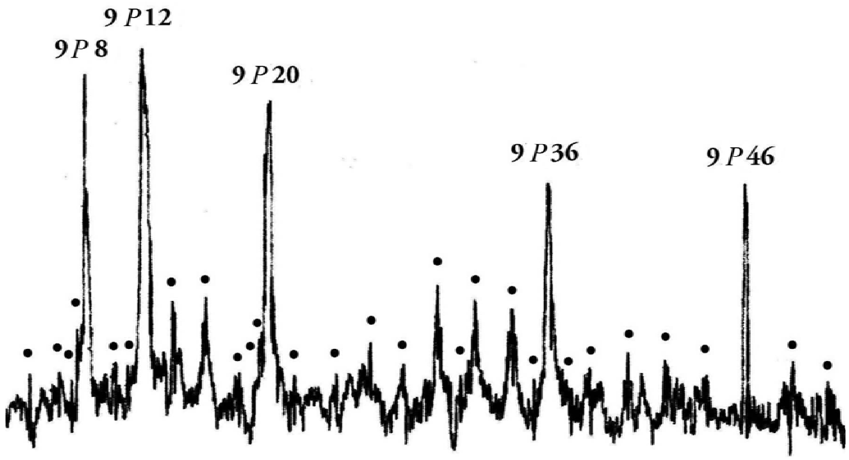

Figure 1. Optoacoustic scan of N_2H_4 recorded with the 9*P* branch of the CO_2 laser. Intense absorption signals are labeled with their corresponding CO_2 pump lines while all other absorptions corresponding to CO_2 laser lines are indicated by dots.

EXPERIMENTAL DETAILS

To search for new short-wavelength FIR laser lines, a high-resolution carbon dioxide (CO_2) pump laser [22] and a low-loss Fabry-Perot FIR cavity, described in detail elsewhere [1, 3], were used. The CO_2 laser radiation was focused into the 2-m long, FIR cavity that utilized an X-V pumping geometry to excite the laser medium. A microphone was placed inside the cavity in order to obtain optoacoustic signals indicating the absorption of CO_2 laser lines by the FIR laser medium [22]. Figure 1 illustrates a typical optoacoustic spectrum with the relative absorption of the molecule in the FIR cavity (in this case N_2H_4) plotted as a function of the CO_2 pump line being used.

The FIR cavity utilized a nearly confocal mirror system with one end mirror mounted on a micrometer to tune the cavity into resonance with the FIR laser radiation. Laser wavelengths were measured with an uncertainty of ± 0.5 μm by scanning over 20 adjacent longitudinal laser modes for a particular FIR laser emission. The intensities of FIR laser emissions were measured with a pyroelectric detector using various filters that attenuate CO_2 laser radiation and help distinguish different FIR wavelengths [1]. The relative polarizations of FIR laser emissions with respect to the CO_2 laser lines were measured with a gold-wire-grid polarizer (1000 lines per inch). The N_2H_4 sample was obtained from Sigma Aldrich while the samples N_2D_4, 98% D_4 enriched; CD_2F_2, 98% D_2 enriched; CH_3OD, 99% D enriched, CH_2DOH, 98% D enriched, and CD_3OH, 99.5% D_3 enriched, were obtained from Cambridge Isotope Laboratories.

RESULTS AND CONCLUSIONS

Table 1 lists eleven FIR laser emissions discovered from optically pumped N_2H_4, CH_3OD, CH_2DOH and CD_3OH. These lines, varying in wavelength from 49.0 to 185.0 μm, are arranged by molecule in order of their CO_2 pump and are given with their polarization measured with respect to the CO_2 laser line, operating pressure and relative intensity. The reported operating pressures are the optimum pressures achieved, however, many emissions worked effectively over a wide range of pressures, sometimes with pressure variations up to ± 10 Pa from the values reported in Table 1. The intensity of the FIR output is given as a listing ranging from very, very strong (VVS) to very weak (VW). The 118.8 μm laser line from optically pumped CH_3OH is considered to be VVS and is expected to provide a power greater than 10 mW when all the parameters (pump laser, FIR resonator, coupling mirror, pressure, etc.) have been optimized. We obtained the relative intensities of the FIR emissions by optimizing the laser cavity to the best of our ability, however, they should be taken only as the best result for this particular experimental setting since the relative intensity values depend on the experimental apparatus used [23]. The lines labeled VS, S, M, W and VW have ranges in power from 10-1 mW, 1-0.1 mW, 0.1-0.01 mW, 0.01-0.001 mW and below 1 μW, respectively. Table 1 also reports for the first time the relative polarizations measured for eight previously observed FIR laser emissions from optically pumped N_2H_4, CH_3OD and CD_2F_2. These lines are given with their previously reported wavelengths and respective references.

Table 1. New FIR laser emissions and polarizations from optically pumped N_2H_4, CH_3OD, CD_2DOH, CD_3OH and CD_2F_2.

CO_2 Pump	Wavelength (μm)	Pressure (Pa)	Relative Intensity	Relative Polarization	Ref.
N_2H_4					
9*P*14	115.8	37.3	M	⊥	New
9*P*36	134.736	33.3	W	⊥	[24]
10*R*40	96.342	36.5	S	⊥	[8]
10*R*36	64.0	43.9	M	‖	New
	83.6	44.7	W	⊥	New
10*P*6	134.922	52.5	M	⊥	[25]
10*P*44	94.489	25.3	S	‖	[24]
	122.231	23.9	VS	⊥	[24]
10*P*56	192.616	14.9	VVS	‖	[24]
CH_3OD					
9*R*16	54.0	25.3	M	‖	New
9*R*6	69.5	25.3	W	⊥	[26]
9*P*6	183.3	21.3	W	⊥	New
10*R*42	90.1	22.1	W	‖	New
CH_2DOH					
9*P*32	56.0	14.5	W	⊥	New
9*P*40	86.5	26.5	W	⊥	New
10*P*46	49.0	13.5	M	⊥	New
	56.9	13.5	M	‖	New
CD_3OH					
10*R*24	185.0	20.3	W	⊥	New
CD_2F_2					
10*R*36	120.5	47	W	⊥	[12]

For CH_3OD, the new 183.3 μm line discovered with the 9*P*6 CO_2 pump line was observed at the same offset as the 134.7 μm line. This offset was different from that used to pump the 230.11 μm line. Also, the 182.1 μm line reported previously [27] was not observed in this work.

Table 2 lists the improved detection of previously observed FIR laser emissions. Many of the reported lines increased in intensity by at least a factor of 10. Four lines reported in Table 2 were observed with a different polarization than previously reported and are denoted accordingly.

Table 2. Improvement in previously observed laser emissions from optically pumped N_2H_4, CH_3OD, CD_3OH and CD_2F_2.

CO_2 Pump	Wavelength (μm)	Observed Relative Polarization	Pressure (Pa)	Relative New	Intensity Old	Ref.
N_2H_4						
9P36	101.756	‖	45.2	S	M	[24]
	134.736	⊥	33.3	M	W	[24]
10P6	134.922	⊥	52.5	M		[25]
10P16	81.229	⊥	47.5	VS	M	[9, 25]
CH_3OD						
9R16	70.3	⊥[a]	36.9	M	M	[26]
9R8	47.65	‖	20.0	VS		[28]
	57.151	⊥	30.8	VS	S	[29, 30]
9P6	134.7	‖[b]	20.0	S	M	[30]
9P32	88.72	⊥	26.6	W		[28]
	110.7	‖[b]	15.3	VW	VW	[27]
CD_3OH						
10R34	182.4	⊥	33.3	S	M	[31]
CD_2F_2						
10R14	187.819	‖[b]	36.0	S	S	[12]

[a] Previously observed in the parallel polarization
[b] Previously observed in the perpendicular polarization

Tables 1 and 2 show that most of the FIR laser emissions discovered or observed to improve with this system were below 150 micron. Although designed for short-wavelengths, numerous FIR laser emissions with wavelengths above 150 μm have also been observed with this system. Prior to this investigation, the longest laser emission produced by this cavity was the 253.720 μm line of CD_3OH, pumped by the 10*R*36 emission of the CO_2 laser. In this work, several FIR laser emissions were observed with longer wavelengths, including two relatively strong emissions above 300 micron (the 301.275 μm emission of N_2H_4 using the 10*R*12 CO_2 pump line and the 320.597 μm emission of CD_2F_2 using the 10*R*44 CO_2 pump line).

The only FIR laser emission observed from N_2D_4 in this work was a weak signal at 159.5 μm, obtained using the 9*P*36 CO_2 pump line. This FIR laser emission occurred at the strongest absorption signal in the N_2D_4 optoacoustic scan. One possible reason for the lack of FIR laser emissions from N_2D_4 became apparent when its optoacousic scans were compared with those from N_2H_4, the N_2D_4 optoacoustic scans were significantly weaker than those of its parent species. Although N_2D_4 and CD_2F_2 did not appear to be efficient sources of new short-wavelength laser emissions, these molecules might still be good candidates for producing OPML emissions provided different pump sources, operating in a different portion of the spectral region (such as the N_2O laser), are used.

In conclusion, this OPML system has been used to observe over 90 FIR laser emissions from those isotopes (30 from N_2H_4, 1 from N_2D_4, 28 from CH_3OD, 20 from CH_2DOH and 10 from CD_2F_2; CD_3OH was not included in this list because it had previously been investigated with this system [1]). Eleven of the reported laser emissions are new and range in wavelength from 49.0 to 185.0 μm. Also measured for the first time were the relative polarizations of eight known FIR laser emissions from optically pumped N_2H_4, CH_3OD and CD_2F_2. The effectiveness of the X-V pump geometry in stimulating short-wavelength FIR laser emissions has been further demonstrated with the discovery of these emissions as well as in the improvement in output power observed from nine known laser emissions.

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REFERENCES

1. M. Jackson, E. M. Telles, M. D. Allen, K. M. Evenson: *Appl. Phys. B* **72**, 815 (2001).
2. K. M. Evenson, Q. Sanford, C. Smith, D. Sutton, J. Sullivan, E. Vershure, M. Jackson: *Appl. Phys. B* **74**, 613 (2002).
3. M. Jackson, H. Hockel, M. Lauters, E. C. C. Vasconcellos, M. D. Allen, K. M. Evenson: *IEEE J. Quantum Electron.* **38**, 429 (2002).
4. H. Hockel, M. Lauters, M. Jackson, J. C. S. Moraes, M. D. Allen, K. M. Evenson: *Appl. Phys. B* **73**, 257 (2001).
5. Li-Hong Xu and G. Moruzzi: *J. Mol. Spectrosc.* **204**, 48 (2000).
6. A. Bertolini, G. Carelli, A. Moretti, G. Moruzzi, F. Strumia: *IEEE J. Quantum Electron.* **35**, 12 (1999).
7. A. Bertolini, G. Carelli, A. Moretti, G. Moruzzi, F. Strumia: *Int. J. Infrared Millim. Waves* **20**, 759 (1999).
8. E. C. C. Vasconcellos, M. D. Allen, L. R. Zink, K. M. Evenson: *Int. J. Infrared Millim. Waves* **21**, 725 (2000).
9. E. C. C. Vasconcellos, S. C. Zerbetto, L. R. Zink, K. M. Evenson: *J. Opt. Soc. Am. B.* **15**, 1839 (1998).
10. A. S. Sheyrev, S. F. Dyubko, M. N. Efimenko, L. D. Fesenko: *Zh. Prikl. Spektrosk.* **42**, 480 (1985).
11. M. S. Tobin, J. P. Sattler, T. W. Daley: *IEEE J. Quantum Electron.* **18**, 79 (1982).
12. E. C. C. Vasconcellos, F. R. Petersen, K. M. Evenson: *Int. J. Infrared Millim. Waves* **2**, 705 (1981).
13. S. F. Dyubko, V. A. Svich, L. D. Fesenko: *JETP Lett.* **16**, 418 (1972).
14. E. C. C. Vasconcellos, S. C. Zerbetto, L. R. Zink, K. M. Evenson: *Int. J. Infrared Millim. Waves* **21**, 731 (2000).
15. R. M. Lees: *Int. J. Infrared Millim. Waves* **21**, 1787 (2000).
16. E. M. Telles, L. R. Zink, K. M. Evenson: *Int. J. Infrared Millim. Waves* **20**, 741 (1999).
17. D. Pereira, J. C. S. Moraes, E. M. Telles, A. Scalabrin, F. Strumia, A. Moretti, G. Carelli, C. A. Massa: *Int. J. Infrared Millim. Waves* **15**, 1 (1994).
18. E. C. C. Vasconcellos and S. C. Zerbetto: *Int. J. Infrared Millim. Waves* **15**, 889 (1994).
19. D. A. Jennings: *Int. J. Infrared Millim. Waves* **1,** 117 (1980).
20. J. A. Facin, D. Pereira, E. C. C. Vasconcellos, A. Scalabrin, C. A. Ferrari: *Appl. Phys. B* **48,** 245 (1989).
21. A. Bertolini, G. Carelli, N. Ioli, C. A. Massa, A. Moretti, F. Strumia: *Int. J. Infrared Millim. Waves* **18,** 1281 (1997).
22. E. M. Telles, H. Odashima, L. R. Zink, K. M. Evenson: *J. Mol. Spectrosc.* **195**, 360 (1999).
23. D. T. Hodges: *Infrared Phys.* **18,** 375 (1978).
24. E. C. C. Vasconcellos, L. R. Zink, G. P. Galvao, K. M. Evenson: *IEEE J. Quantum Electron.* **30**, 2401 (1994).
25. H. E. Radford, K. M. Evenson, F. Matsushima, L. R. Zink, G. P. Galvao, T. J. Sears: *Int. J. Infrared Millim. Waves* **12**, 1161 (1991).
26. M. W. Lund and J. A. Davis: *IEEE J. Quantum Electron.* **15,** 537 (1979).
27. Y. C. Ni and J. Heppner: *Opt. Commun.* **32,** 459 (1980).
28. J. K. Vij, F. Hufnagel, M. Helker, C. J. Reid: *IEEE J. Quantum Electron.* **22,** 1123 (1986).
29. S. Kon, T. Yano, E. Hagiwara, H. Hirose: *Jpn. J. Appl. Phys.* **14,** 1861 (1975).
30. B. L. Bean and S. Perkowitz: *Opt. Lett.* **1,** 202 (1977).
31. E. J. Danielewicks and C. O. Weiss: *IEEE J. Quantum Electron.* **14,** 458 (1978).