New far-infrared hydrazine laser lines and their frequencies

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We have discovered 74 far-infrared laser lines pumped by regular and sequence lines of a cw CO_2 laser. The wavelengths range from 49.2 to 708.3 μm. These new lines are to our knowledge the shortest-wavelength far-infrared lines yet observed lasing in hydrazine. Frequency, pump offset, and relative polarization were measured for most of these new lines.

1. INTRODUCTION

Hydrazine (N_2H_4) is a promising far-infrared (FIR) laser molecule for generating FIR radiation. A total of 75 FIR laser lines have been obtained from hydrazine pumped by CO_2 lasers, most at wavelengths longer than 200 μm, and 6 other lines from hydrazine pumped by a N_2O laser.[1] Of these, only 14 lines are pumped by the 10*R* branch of the CO_2 laser.

We report 74 new FIR laser lines from hydrazine, most of them of wavelengths shorter than 200 μm, pumped by regular and nonregular lines of a CO_2 laser. A pair of frequency-stabilized CO_2 lasers was used as standards for heterodyne frequency measurements of 40 of the new laser lines. We also report the relative polarization, relative intensity, and operating pressure for most of these lines, along with the measurements of the pump offset for 61 lines.

2. EXPERIMENT

A. Wavelength Measurements

The pump laser is a 1.5-m-long, cw CO_2 laser with a 171-line/mm grating for the 9-μm band or a 163-line/mm grating for the 10-μm band. Exceptional frequency discrimination of the gratings plus the ribbed laser tube permit the operation of the laser on nonregular CO_2 laser lines; regular and nonregular laser lines have powers up to 30 and 11 W, respectively. The FIR laser cavity consists of a rectangular waveguide with the top and bottom walls made of oxygen-free copper 35 mm wide, and the vertical walls are made of window glass 6 mm high.[2] The cavity is 2 m long with gold-coated flat copper mirrors located a few millimeters from each end of the waveguide. The lowest-loss mode has the laser electric field parallel to the metal walls (i.e., horizontal). The pump radiation is focused into the FIR cavity through a 1-mm-diameter hole in the center of the fixed end mirror. The other end mirror is fastened to a micrometer and can be moved longitudinally to tune the cavity into resonance with the FIR laser lines. The cavity thus serves as an interferometer for wavelength measurements. The FIR laser power is coupled out through a movable 5-mm-diameter 45° copper mirror inserted into the waveguide perpendicular to the laser axis. By adjusting the position of the coupling mirror, we can maximize the FIR laser power leaving the cavity through a silicon Brewster-angle window in the opposite wall. The FIR laser radiation is focused onto a metal–insulator–metal (MIM) diode used as a detector. We obtained the wavelengths of the new lines by measuring the FIR cavity length change for a change of 10 wavelengths.

B. Frequency Measurements

Two frequency-stabilized CO_2 lasers and a microwave source were used to measure the frequency of the FIR laser line. These, plus the unknown FIR radiation, were mixed on a MIM point contact diode.[3] The beat note, with a typical width of 20 kHz, generated by the MIM diode is amplified and displayed on a spectrum analyzer with a peak-hold feature that records the beat note as the FIR laser is tuned over its gain curve. The center of this recording is then marked with an oscillator, whose frequency is counted. The FIR frequency is then determined by the equation

$$\nu_{\mathrm{FIR}} = |\nu_1 - \nu_2| \pm \nu_{\mathrm{beat}} \pm \nu_{\mu\mathrm{wave}}\,, \tag{1}$$

where ν_1 and ν_2 are the CO_2 laser frequencies, $\nu_{\mu\mathrm{wave}}$ is the frequency of the microwave source, and ν_{FIR} is the laser frequency to be measured. ν_1, ν_2, and $\nu_{\mu\mathrm{wave}}$ are chosen so that

$$0 < |\nu_{\mathrm{beat}}| < 1.5\ \mathrm{GHz}\,. \tag{2}$$

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Table 1. New N_2H_4 Far-Infrared Laser Lines

Pump Line CO_2 Laser[a]	Wavelength (μm)	Offset (MHz)	Pressure Pa (mTorr)	Relative Polarization	Relative Intensity (mV)[b]	Pump Power (W)
9*R*(50)	65.842	−9	52(400)	‖	0.3	8.0
9*R*(46)	154.065	−2	11(80)	‖	0.5	15.0
	454.7	−2	33(250)	‖	0.2	15.0
9*R*(42)	349.345	—	20(105)	⊥	4.0	25.0
9*R*(36)	101.618	−38	27(200)	‖	1.0	30.0
9*R*(34)	283.947	—	13(100)	‖	6.0	30.0
9*R*(26)	327.102[c]	−13	20(105)	‖	1.0	27.0
9*R*(14)	85.717	−50	27(200)	‖	2.0	25.0
9*R*(10)	249.092[c]	−20	20(150)	‖	0.6	20.0
9*R*(08)	81.099	−12	33(250)	‖	1.5	15.0
9*R*(04)	76.511	+40	13(100)	‖	0.3	10.0
	125.7	—	20(250)	‖	0.2	10.0
9*SP*(11)	85.9	—	13(100)	‖	2.0	7.0
9*P*(08)	708.3	—	20(150)	‖	0.4	10.0
9*P*(14)	90.373	−32	52(400)	‖	2.5	25.0
9*P*(16)	84.765	+8	20(150)	‖	0.2	25.0
	90.724	−45	20(150)	‖	1.5	25.0
9*SP*(13)	103.950	−12	52(450)	‖	6.0	7.0
9*P*(30)	156.107	+28	20(150)	‖	0.3	28.0
9*P*(32)	73.868	+28	40(300)	‖	1.0	27.0
p*P*(46)	160.628	−7	27(200)	‖	3.0	18.0
	312.027	−7	27(200)	‖	2.5	18.0
9*P*(50)	142.462	+43	20(150)	‖	2.5	15.0
9*P*(52)	121.199	−45	27(200)	‖	1.0	13.0
9*P*(56)	182.346	−32	20(150)	‖	1.5	12.0
10*R*(54)	109.849	−19	21(160)	‖	0.4	5.5
	128.077	+19	33(250)	‖	1.6	5.5
10*R*(52)	142.335	+40	43(320)	‖	1.5	6.0
10*R*(50)	59.544	−16	117(880)	‖	1.0	
	61.9	—	96(720)	‖	0.6	17.0
	113.621[d]	+7	29(220)	‖	1.2	17.0
	113.621[d]	+7	29(220)	‖	1.2	17.0
	183.254	+7	29(220)	⊥	0.2	17.0
10*R*(48)	109.378	+10	40(300)	‖	0.3	20.0
10*R*(44)	113.064	−22	44(330)	‖	1.5	18.0
10*R*(42)	84.417	+44	44(320)	‖	0.5	18.0
	89.677	−23	20(250)	‖	0.3	18.0
10*R*(40)	201.796	−36	64(490)	‖	3.0	
10*R*(38)	235.559[c]	—	25(190)	‖	5.0	22.0
10*R*(36)	109.164	−14	25(190)	‖	0.2	25.0
	160.448	+44	33(250)	‖	1.5	21.0
	312.027	+44	37(280)	⊥	1.0	21.0
10*R*(34)	143.974	+41	40(300)	⊥	3.0	21.0
	153.4	—	29(220)	‖	5.0	21.0
	218.562	+44	40(300)	‖	4.0	21.0
10*R*(30)	264.715	−10	33(250)	‖	1.0	21.0
10*R*(28)	153.324	+42	28(210)	‖	2.0	20.0
10*SR*(27)	161.146	+7	37(280)	‖	2.0	9.0
10*SR*(23)	91.539	+26	32(240)	‖	3.5	11.0
	109.277	−28	25(190)	‖	5.0	11.0
	267.4	+47	32(240)	‖	0.6	11.0
10*R*(18)	107.416	—	36(270)	‖	0.1	16.0
	116.7	−33	40(300)	‖	0.1	16.0
10*SR*(21)	319.249	—	27(200)	‖	4.0	9.0
10*SR*(17)	186.159	+19	20(150)	‖	6.0	11.0
10*HR*(14)	151.635	−30	13(100)	‖	0.6	
	190.353	−8	13(100)	⊥	0.2	
10*SR*(11)	125.885[d]	+36	13(100)	‖	1.0	6.0
	125.885[d]	+36	13(100)	‖	1.0	6.0
	198.488	—	11(80)	‖	0.03	6.0
10*SR*(09)	266.128	0	20(150)	⊥	5.0	8.0
	464.264	0	19(140)	‖	6.0	8.0
10*R*(04)	58.598	—	108(810)	‖	0.2	15.0
	116.466	+39	39(290)	‖	6.0	15.0

(*Table Continued*)

Table 1. Continued

Pump Line CO_2 Laser[a]	Wavelength (μm)	Offset (MHz)	Pressure Pa (mTorr)	Relative Polarization	Relative Intensity (mV)[b]	Pump Power (W)
10*P*(02)	74.627	—	21(160)	‖	0.1	8.0
	165.480	−11	23(170)	‖	0.3	8.0
10*P*(04)	49.2	−36	24(180)	‖	0.1	10.0
	78.1	−33	23(170)	‖	0.1	10.0
	90.307	—	27(200)	⊥	0.03	10.0
	114.183	+42	28(210)	‖	1.5	10.0
	124.090	—	39(290)	‖	0.2	10.0
	142.830	—	20(150)	‖	0.2	10.0
	186.1	+42	24(180)	⊥	0.02	
10*P*(10)	206.692	+37	40(300)	‖	0.4	9.0
10*P*(12)	157.133	−43	24(180)	‖	0.5	7.0
10*P*(30)	111.234	−8	13(100)	‖	0.1	
10*SP*(29)	185.572	−12	20(150)	‖	2.0	

[a] *S*, sequence line; *H*, hot-band line.
[b] 119 μm from CH_3OH had relative intensity of ~8 mV in the same cavity under similar conditions.
[c] Doublets; see Table 2.
[d] Previously reported; see Ref. 1.

Table 2. Far-Infrared Frequency Measurements of the New Optically Pumped N_2H_4 Laser Lines

Pump Line CO_2 Laser	Measured Frequency (MHz)[a]	Calculated Wavelength (μm)[b]	Wave Number (cm^{-1})	Pump Line CO_2 Laser	Measured Frequency (MHz)[a]	Calculated Wavelength (μm)[b]	Wave Number (cm^{-1})
10*R*(04)	5 116 059.9	58.598	170.6534	10*R*(54)	2 340 717.5	128.077	78.0779
10*R*(50)	5 034 814.5	59.544	164.9433	10*R*(52)	2 106 238.3	142.335	70.2565
9*R*(50)	4 553 228.0	65.842	151.8793	9*P*(50)	2 104 368.9	142.462	70.1942
9*P*(32)	4 058 513.9	73.868	135.3775	10*P*(04)	2 098 942.5	142.830	70.0132
10*P*(02)	4 017 213.1	74.627	133.9998	10*R*(34)	2 082 274.2	143.974	69.4572
9*R*(04)	3 918 281.0	76.511	130.6998	10*HR*(14)	1 977 072.4	151.635	65.9480
9*R*(08)	3 696 638.2	81.099	123.3066	10*R*(28)	1 955 291.8	153.324	65.2215
10*R*(42)	3 551 318.2	84.417	118.4592	9*R*(46)	1 945 888.1	154.065	64.9078
9*P*(16)	3 536 744.1	84.765	117.9731	9*P*(30)	1 920 424.5	156.107	64.0585
9*R*(14)	3 497 481.1	85.717	116.6663	10*P*(12)	1 907 887.0	157.133	63.6403
10*R*(42)	3 343 021.8	89.677	111.5112	10*R*(36)	1 868 475.0	160.448	62.3256
10*P*(04)	3 319 710.8	90.307	110.7336	9*P*(46)	1 866 375.4	160.628	62.2556
9*P*(14)	3 317 269.0	90.373	110.6523	10*SR*(27)	1 860 374.8	161.146	62.0554
9*P*(16)	3 304 457.8	90.724	110.2244	10*P*(02)	1 811 655.9	165.480	60.4303
10*SR*(23)	3 275 035.8	91.539	109.2434	9*P*(56)	1 644 081.4	182.346	54.8407
9*R*(36)	2 950 180.8	101.618	98.4074	10*R*(50)	1 635 937.6	183.254	54.5690
9*SP*(13)	2 884 000.7	103.950	96.1999	10*SP*(29)	1 615 503.5	185.572	53.8874
10*R*(18)	2 790 942.8	107.416	93.0958	10*SR*(17)	1 610 436.0	186.156	53.7184
10*R*(36)	2 746 267.9	109.164	91.6056	10*HR*(14)	1 574 927.0	190.353	52.5339
10*SR*(23)	2 743 410.5	109.277	91.5103	10*SR*(11)	1 510 382.3	198.488	50.3809
10*R*(48)	2 740 883.2	109.378	91.4260	10*R*(40)	1 485 618.5	201.796	49.5549
10*R*(54)	2 729 129.8	109.849	91.0340	10*P*(10)	1 450 431.1	206.692	48.3812
10*P*(30)	2 695 149.6	111.234	89.9005	10*R*(34)	1 371 660.8	218.562	45.7537
10*R*(44)	2 651 522.1	113.064	88.4453	9*R*(10)	1 203 541.3	249.092	40.1458
10*R*(50)	2 638 540.7	113.621	88.0122[c]	10*R*(30)	1 132 510.3	264.715	37.7765
10*R*(50)	2 638 537.7	113.621	88.0121[c]	10*SR*(09)	1 126 495.9	266.128	37.5759
10*P*(04)	2 625 546.4	114.183	87.5788	9*R*(34)	1 055 803.2	283.947	35.2178
10*R*(04)	2 574 085.5	116.466	85.8622	10*R*(36)	960 791.1	312.027	32.0485
9*P*(52)	2 473 562.9	121.199	82.5092	10*SR*(21)	939 054.3	319.249	31.3235
10*P*(04)	2 415 908.4	124.090	80.5860	9*R*(26)	916 511.7	327.102	30.5715
10*SR*(11)	2 381 482.4	125.885	79.4377[c]	10*SR*(09)	645 737.5	464.264	21.5395
10*SR*(11)	2 381 478.9	125.885	79.4376[c]				

[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] Doublets.

C. Offset Measurements

To measure the offset between the pump frequency and the center frequency of the CO_2 laser line, a frequency-stabilized CO_2 laser set to the same laser line as the pump is mixed with the pump frequency in a MIM diode. The radiation of a few gigahertz from a microwave source is added to the MIM whenever the pump line is a sequence line to make up the difference in frequency between the regular and sequence lines. The MIM diode generates a beat note

$$\nu_{\text{beat}} = |\nu_{\text{ref}} - \nu_{\text{pump}}| \pm n\nu_{\mu\text{wave}}\,, \tag{3}$$

where ν_{ref} is the frequency of the reference CO_2 laser, ν_{pump} is the pump frequency, $\nu_{\mu\text{wave}}$ is the frequency of the microwave source, and n is the harmonic order generated by the diode. In the case of regular lines the beat note frequency is the pump offset frequency. We can easily determine the sign of the unknown frequency by slightly varying the frequency of the pump laser and the microwave source and noting the relative frequency change of the beat note.

3. CONCLUSIONS

The 74 new FIR laser lines generated by hydrazine are listed in Table 1 together with their optimum pressure, relative polarization, offset, CO_2 pump power, and relative intensity. Their wavelengths are in the range 49.2–708.3 μm. The intensities are proportional to the rectified voltage on the MIM diode. Several new laser lines were very strong, with intensities comparable with that obtained for the 119-μm laser line of methanol observed in the same FIR cavity. The majority of the laser lines have wavelengths shorter than 200 μm. Nineteen of the laser lines have wavelengths shorter than 100 μm; the shortest is the 49.2-μm line pumped by $10P(04)$.

Table 2 lists the frequency measurements in the range 0.6–5.1 THz (464.3–58.6 μm). Two of the new lines were in fact doublets: the 113.6-μm line, pumped by $10R(50)$, and the 125.9-μm line, pumped by $10SR(11)$.

The great success of hydrazine as a FIR laser molecule is due to its strong absorption band in the 10-μm region, associated with the NH_2 antisymmetric wagging motion of the molecule,[4] and to its fairly large electric dipole moment (1.8 D).[5,6] One can understand the richness of the rovibrational spectrum by considering the splittings caused by the inversion of the two NH_2 groups and the internal rotation about the N—N bond.[7]

In conclusion, we have increased the number of hydrazine lines to 155, and more than two thirds of the frequencies of these have now been measured. Thirteen of the new lines were pumped by high-J CO_2 laser lines ($J > 48$), and sixteen of them were pumped by either sequence or hot-band laser lines. With these results we conclude that the N_2H_4 is a very good FIR laser medium not only because of the great number of laser lines produced but also because many of them are strong and at high frequency ($\lambda < 200$ μm), in contrast with those reported in the earliest works on hydrazine.[1,8] They will be useful for both atomic and molecular spectroscopy.

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