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New FIR laser lines from hydrazine and assignments

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ABSTRACT Our new waveguide pulsed CO_2 laser, with peak powers above 1 kW, has allowed us to observe 24 new far-infrared laser lines emitted by hydrazine. Each of them is characterized in wavelength, relative polarization, intensity, optimum operating pressure and pump offset from the center of the exciting CO_2 line. These new laser emissions either form pairs sharing the same pump line, or complete such pairs with lines known from the literature. In the latter case, we have measured the relative polarization and offset of the partner lines whenever they were not reported in the literature. The availability of laser systems with two emission lines orthogonally polarized and sharing the same upper level is expected to facilitate the assignment work. We present complete assignments for four FIR laser emissions, and we propose J and K values for 12 further laser systems.

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1 Introduction

Hydrazine (N_2H_4), with hundreds of lasing lines, is one of the most prolific known laser-active molecules in the far-infrared (FIR) region. It was first reported as a lasing medium in 1974 by Dyubko et al. [1]. A review of N_2H_4 laser lines can be found in [2] and other lines were successively reported in [3–5]. The rovibrational spectrum of hydrazine is complicated by the presence of three large-amplitude vibrational motions: the internal torsional rotation around the N–N bond and the symmetric and antisymmetric amino-wagging motions. The fundamental of the antisymmetric amino-wagging mode lies in the same spectral region of the CO_2 laser emission spectrum, so that most of the observed FIR laser lines emitted by hydrazine are excited by CO_2 laser emissions. The existence of eight nonsuperimposable conformations of the N_2H_4 molecule, which can be interconverted by the three large-amplitude vibrational motions, makes a systematic assignment of the spectrum and, in particular, the correct identification of a laser system, a very difficult task, so that only few assignments have been possible until now [6–8].

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While the determination of the symmetry species involved in a laser system remains a difficult task, it is very often possible to determine the J and K quantum numbers involved in the FIR laser emissions. This usually happens when the system comprises two FIR emissions polarized perpendicularly to each other, and excited by the same CO_2 line at the same offset [6]. This has led us to search for new N_2H_4 FIR laser emissions which either form pairs polarized perpendicularly to each other, or share the CO_2 pump and offset with known lines, thus completing such pairs. We have observed 24 new lines, and measured the relative polarization of many previously observed lines whose polarization was not reported in the literature. We have thus built a list of many pairs of FIR laser lines that are good candidates for assignment. However, due to the incompleteness of the available analyses of the IR spectrum of hydrazine we are able to give 'complete assignments' (i.e. including the symmetry species and the vibrational quantum numbers) only for two of these pairs.

2 Experiment and results

Our experimental apparatus consists, basically, of a pump CO_2 laser and a Fabry–Perot cavity used as FIR laser resonator. Our waveguide CO_2 laser has a continuous tunability of 160 MHz around each emission. A diffraction grating of 150 lines/mm selects the CO_2 emission line, while the fine frequency tuning is achieved by shifting the ZnSe output mirror by means of a piezo-electric transducer (PZT), thus fine tuning the cavity length. The laser operates in the pulsed regime, driven by a new solid-state power supply based on the discharge of a capacitor driven by an IGBT transistor [9]. The pulse duration can be adjusted between 15 and 40 μs, and the repetition rate between 500 and 1000 Hz. The output peak power on the strongest lines is above 1 kW. The FIR laser resonator is a nearly confocal 1-m-long Fabry–Perot cavity with a 10-cm inner diameter, terminated by two gold-coated copper spherical mirrors with a focal length of 58 cm. The pump radiation is injected into the FIR resonator through a 2-mm axial hole in the front mirror, vacuum sealed by a ZnSe antireflection-coated window. The second mirror is mounted on a precision screw, equipped with an optical encoder, used both to tune the cavity length into resonance with the FIR radiation and to measure the emitted wavelength. A fraction of the FIR power is coupled out of the cavity through a silicon window after reflection on an elliptical mirror obtained by cut-

ting a 6-mm-diameter copper rod at 45°. This mirror can be translated perpendicularly to the cavity axis in order to optimize the output power for each FIR wavelength. The FIR output radiation is detected by a Golay cell. An electret microphone is located inside the FIR laser cavity in order to detect optoacoustical signals. If the intensity of the CO_2 radiation is modulated at an acoustical frequency (in our case the modulation is due to the pulsed regime), an optoacoustical signal is observed at each coincidence of the CO_2 laser frequency with a hydrazine absorption transition. When a new optoacoustical signal is detected, the FIR cavity length is scanned for searching and characterizing new possible FIR laser lines.

The investigated lines are listed in Table 1, where we report for each of them: the CO_2 pump line, the measured wavelength, the offset relative to the center frequency of the pump radiation, the relative intensity, the polarization relative to the CO_2 radiation and the optimum operation pressure. The wavelengths have been measured by varying the cavity length by

translating the moving mirror for about 20 modes. The accuracy of these measurements is approximately $\pm 0.5\,\mu$m, estimated by a calibration procedure against frequency-measured lines. The accuracy of our offset measurements is approximately 10 MHz. Whenever one of our new FIR laser lines forms a pair with a known line whose pump offset is reported in the literature with a better precision, this offset value is attributed to the new line in Table 1. The measured relative intensity is reported as strong (S), medium (M) or weak (W) according to the parameters defined in [10]. According to this notation, after optimization of all the parameters (pump laser, operation pressure, FIR cavity, output coupling, etc.), the power that can be extracted from the FIR laser is larger than 1 mW (S), between 1 mW and 100 µW (M) and below 100 µW (W). The polarization of the FIR laser lines was measured with a mesh polarizer. The column 'Comments' reports either the word 'New' for lines first observed in the present work, or the reference to the work where the line was first reported. In the latter case either the offset from the pump center, or the relative polarization, or both, are presented for the first time in this work.

3   Assignment procedure

Most of the observed far infrared (FIR) laser emissions of hydrazine are excited by CO_2 laser lines which pump the molecule into its first excited antisymmetric amino-wagging state. Due to the spectral complexities that we shall briefly discuss later on in this section, the systematic assignment of the IR absorption spectrum of hydrazine in the $900–1100\,\mathrm{cm}^{-1}$ is less advanced than the corresponding assignment, for instance, of methanol. At the moment, the only published works reporting systematic studies of the infrared spectrum of hydrazine are due to Ohashi et al. [11] and Gulaczyk et al. [12]. These investigations of the antisymmetric amino-wagging fundamental cover the K values up to 13, and exclude transitions between states involving the simultaneous excitation of the ν_{12} and torsional modes. Further, as for all optically excited molecular lasers, a fortuitous coincidence of a CO_2 line with a very weak N_2H_4 absorption can lead to the emission of relatively intense FIR laser lines practically impossible to assign. Thus, we cannot expect a direct comparison to the assigned absorption spectrum of hydrazine (for instance by means of the LaseRitz program [8]) to provide assignments for many of the observed laser systems. Actually, as already noted in [8], only very few laser systems can usually be assigned by this technique. In particular, the lines excited by 9P36, 10R38, 10R12 and 10P44 reported in Table 1, for which we present new measurements of the pump offset, of the relative polarization, or of both, had already been assigned in previous literature. Of the other lines of Table 1, a direct comparison to the assigned absorption spectrum leads to the assignment only of the line excited by 9P50 + 50 MHz. The corresponding assignment is shown in Table 2, together with the FIR emission at $70.194\,\mathrm{cm}^{-1}$, excited by the same pump and already known from literature, but not previously assigned, and the assignments of the two FIR lines pumped by 10R(8) with an offset of -80 MHz which we presented in a recent work [5], and, for comparison, the already known [6–8] assignments of the two FIR lines pumped by the same pump

Pump	Wavelength[a] (µm)	Offset (MHz)	Rel. Int.	Rel. Pol.	Press. (Pa)	Comments
9R26	560.9	−13	M	⊥	12	NEW
9R18	368.862		M	⊥*	27	[2]
9P12	331.299	−20*	S	⊥*	20	[2]
	1055.6	−20	W	∥	20	NEW
	527.873	0*	M	∥*	7	[2]
	331.669	+40*	S	⊥*	20	[2]
	1060.3	+40	W	∥	20	NEW
9P30	121.3	+30	M	⊥	20	NEW
	331.5	+30*	M	∥	20	[2]
9P32	151.6	+28	W	⊥	20	NEW
9P36	185.143		S	⊥*	13	[2]
9P50	116.0	+50	M	⊥	13	NEW
9P52	170.4	−45	W	⊥	20	NEW
10R42	143.8	−23	S	⊥	23	NEW
	312.0	+40	S	⊥	23	NEW
10R40	96.342	−36*	S	⊥*	23	[4]
10R38	734.162		S	⊥*	25	[2]
10R36	159.2	−15	W	⊥	29	NEW
10R34	648.5	0	W	⊥	20	NEW
10R30	170.1	−10	S	⊥	29	NEW
10R26	220	−50	S	⊥	29	NEW
10R24	95.3	+50	W	∥	23	NEW
	330.8	+50	W	⊥	23	NEW
10R18	107.416	−50*	M	∥	23	[2]
10R12	301.275	+20*	S	∥	24	[2]
	68.0	−30	W	∥	24	NEW
	86.6	−30	W	⊥	24	NEW
10R10	646.3	+80	W	⊥	24	NEW
10P12	157.2	−30	M	∥	20	NEW
10P30	134.8	−10	W	⊥	20	NEW
10P40	241.382	+20*	M	∥*	13	[2]
	527.608	+20*	W	⊥*	13	[2]
10P42	314.0	0*	M	∥*	13	[2]
	526.3	0*	M	⊥*	13	[2]
10P44	122.0	−40*	M	⊥*	13	[2]
10P46	174.3	+50	M	⊥	27	NEW
	261.8	+50	M	∥	27	NEW
10P52	161.146	−30*	S	⊥*	23	[2]
	252.0	−30	W	∥	23	NEW
10HP19	127.6		W	⊥	27	NEW

[a] When the wavelength is reported with three digits the measured frequency of the laser line is reported in the reference written in the column 'Comments'.

* New rel. pol., or offset measurement

TABLE 1   New lines and new data for old lines.

Pump	CO_2 pump (N_2H_4 absorption) Waven./cm^{-1}	Pump upper state Pump lower state $\lvert v, J, K$, Symm.$\rangle$	Measured FIR (Calculated FIR) Waven./cm^{-1}	FIR lower state $\lvert v, J, K$, Symm.$\rangle$
9P50 +50 MHz	1016.7209 (1016.7208)	$\lvert aw, 10, 10, E_u\rangle$ $\lvert gr, 10, 9, E_1\rangle$	86.206 (86.209)	$\lvert aw, 9, 9, E_u\rangle$
			70.194191 (70.194)	$\lvert aw, 9, 10, E_u\rangle$
10R8	967.70723 (967.706)	$\lvert aw, 15, 2, B_{2g}^{-}\rangle$ $\lvert gr, 14, 2, A_{2u}^{+}\rangle$	18.738730 (18.740)	$\lvert aw, 15, 1, A_{2u}^{+}\rangle$
			42.750435 (42.752)	$\lvert aw, 14, 1, A_{2u}^{+}\rangle$
10R8 −80 MHz	967.70723 (967.706)	$\lvert aw, 15, 2, B_{1g}^{+}\rangle$ $\lvert gr, 14, 2, A_{1u}^{-}\rangle$	18.694410 (18.696)	$\lvert aw, 15, 1, A_{1u}^{-}\rangle$
			42.772 (42.784)	$\lvert aw, 14, 1, A_{1u}^{-}\rangle$

TABLE 2 Assignments obtained from a direct comparison to the absorption spectrum of hydrazine. Lines reported with eight significant digits have been frequency measured

at zero offset. It is interesting to note that line 10R(8) with zero offset and line 10R(8)–80 MHz excite the two asymmetry doublet components $\lvert gr, 14, 2, A_{2u}^{+}\rangle \rightarrow \lvert aw, 15, 2, B_{2g}^{-}\rangle$ and $\lvert gr, 14, 2, A_{1u}^{-}\rangle \rightarrow \lvert aw, 15, 2, B_{1g}^{+}\rangle$, respectively. Corresponding doublet components are observed also in the FIR laser emissions.

When a direct comparison to the absorption spectrum does not lead to the assignment of a laser system (and this is, by far, the most common case), the J and K values involved in the transitions can often be obtained from the knowledge of the pattern of the sublevels corresponding to the same rotational and vibrational quantum numbers, but belonging to different symmetry species. According to Jon Hougen's treatment [13], states sharing the same rotational and vibrational quantum numbers present the splitting pattern schematically represented in Fig. 1. Taking K-doubling into account, each $\lvert v, J, K\rangle$ level (where v labels the vibrational state) with $K > 0$ splits into 16 sublevels, classified according to the symmetry species of the $G_{16}^{(2)}$ group as A_{1g}^{+}, A_{1u}^{-}, B_{1g}^{+}, B_{1u}^{-}, A_{2g}^{-}, A_{2u}^{+}, B_{2g}^{-}, B_{2u}^{+}, E_{L}^{+}, E_{L}^{-}, E_{U}^{+}, E_{U}^{-}. Of these, the sublevels belonging to E symmetry are doubly degenerate. When the K-doubling is not resolved, the numerical subscripts and the $\pm$ superscripts can be omitted. The largest splittings of the pattern are due to the inversion of the amino groups, which leads to three groups of sublevels. The central group is further split into two subgroups by the Coriolis interaction between the two inversion motions. However, in our analysis, this splitting is neglected following [6, 7]. The symmetry species of each group of sublevels corresponding to the same $\lvert v, J, K\rangle$ level depends on K mod 4, the possibilities being

1. K mod 4 = odd: the two central subgroups belong to A and B symmetry, respectively. The external subgroups belong to E symmetry.
2. K mod 4 = even: the two central subgroups belong to E symmetry, and the external to A and B symmetry, respectively. The upper external subgroup belongs to A symmetry if K mod 4 = 0, to B symmetry if K mod 4 = 2.

The selection rules are: $\Delta J = 0, \pm 1$, $\Delta K = \pm 1$, and $A \leftrightarrow B$ or $E \leftrightarrow E$.

Our analysis follows the assignment procedure of [6, 7]. The energy level of the central (W_c), upper (W_u) and lower
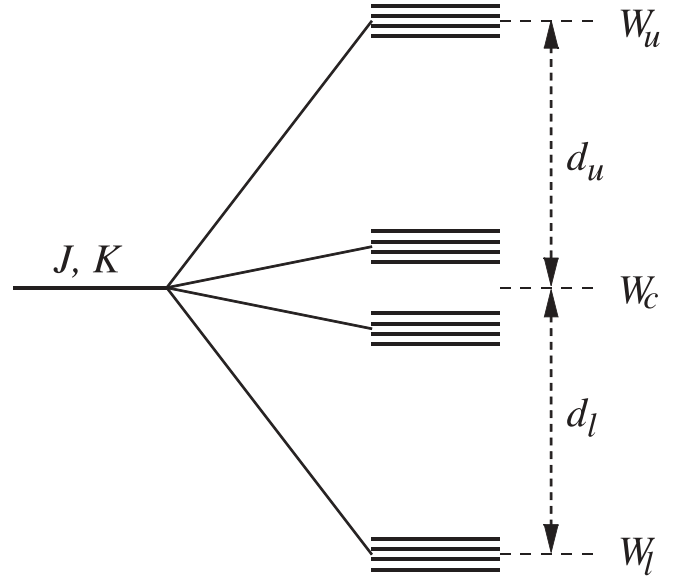
FIGURE 1 Schematic representation of a hydrazine $\lvert J, K\rangle$ multiplet

(W_l) subgroups can be written as:

$$W_c \approx W_v + B_v J(J+1) + (A-B)_v K^2 \tag{1}$$
$$W_u \approx W_c + d_u \tag{2}$$
$$W_l \approx W_c - d_l . \tag{3}$$

The most accurate values available for the molecular parameters are:

$$(A-B)_v = 120.516 \, \text{GHz} \tag{4}$$
$$B_v = 24.0751 \, \text{GHz} . \tag{5}$$

The d_u and d_l parameters are J- and K- dependent, but, as a first approximation, we can assume the average values of:

$$d_u = 197.8 \, \text{GHz} \tag{6}$$
$$d_l = 203.8 \, \text{GHz} \tag{7}$$

If two FIR laser lines of frequencies ν_1 and ν_2 are excited by the same pump transition with the same offset, they must share the same upper level (unless cascade effects are present). Thus, their lower levels must belong to the same symetry

Sys.	Pump + offset (MHz)	λ_{FIR} (μm)	Rel. pol.	Ref.	J K	FIR transition
#1	9R(26)	560.9	$\perp$	New	8	$\vert 8, 2\rangle \to \vert 8, 1\rangle$
	−13	327.102	$\parallel$	[2]	2	$\vert 8, 2\rangle \to \vert 7, 1\rangle$
#2	9P(12)	331.669	$\perp$	[2]	13	$\vert 13, 1\rangle \to \vert 12, 0\rangle$
	+40	1060.3	$\parallel$	New	1	$\vert 13, 1\rangle \to \vert 13, 0\rangle$
#3	9P(12)	331.299	$\perp$	[2]	13	$\vert 13, 1\rangle \to \vert 12, 0\rangle$
	−20	1055.6	$\parallel$	New	1	$\vert 13, 1\rangle \to \vert 13, 0\rangle$
#4	9P(52)	170.4	$\perp$	New	15	$\vert 15, 7\rangle \to \vert 15, 6\rangle$
	−45	121.199	$\parallel$	[2]	7	$\vert 15, 7\rangle \to \vert 14, 6\rangle$
#5	10R(42)	143.8	$\perp$	New	26	$\vert 26, 10\rangle \to \vert 26, 9\rangle$
	−23	89.67	$\parallel$	[2]	10	$\vert 26, 10\rangle \to \vert 25, 9\rangle$
#6	10R(36)	159.2	$\perp$	New	18	$\vert 18, 9\rangle \to \vert 18, 8\rangle$
	−15	109.164	$\parallel$	[2]	9	$\vert 18, 9\rangle \to \vert 17, 8\rangle$
#7	10R(34)	648.5	$\perp$	New	17	$\vert 17, 3\rangle \to \vert 17, 2\rangle$
	0	234.0	$\parallel$	[2]	3	$\vert 17, 3\rangle \to \vert 16, 2\rangle$
#8	10R(30)	170.1	$\perp$	New	13	$\vert 13, 6\rangle \to \vert 12, 5\rangle$
	−10	264.715	$\parallel$	[2]	6	$\vert 13, 6\rangle \to \vert 13, 5\rangle$
#9	10R(10)	646.3	$\perp$	New	9	$\vert 9, 3\rangle \to \vert 9, 2\rangle$
	+80	335.1	$\parallel$	[3]	3	$\vert 9, 3\rangle \to \vert 8, 2\rangle$
#10	10P(46)	174.3	$\perp$	New	12	$\vert 12, 6\rangle \to \vert 11, 5\rangle$
	+50	261.8	$\parallel$	New	6	$\vert 12, 6\rangle \to \vert 12, 5\rangle$
#11	10P(52)	161.146	$\perp$	[2]	14	$\vert 14, 6\rangle \to \vert 13, 5\rangle$
	−30	252.0	$\parallel$	New	6	$\vert 14, 6\rangle \to \vert 14, 5\rangle$
#12	10HP(19)	127.6	$\perp$	New	18	$\vert 18, 11\rangle \to \vert 18, 10\rangle$
	0	93.3	$\parallel$	[2]	11	$\vert 18, 11\rangle \to \vert 17, 10\rangle$

TABLE 3   Possible J and K values for some FIR laser pairs in hydrazine

species because of the selection rules $A \leftrightarrow B$ or $E \leftrightarrow E$. If the two FIR laser lines are polarized perpendicularly to each other, the lower levels must have consecutive J values. Thus the two FIR laser transitions can be labeled as:

$$\nu_1 : \vert J, K\rangle \to \vert J, K-1\rangle \tag{8}$$

$$\nu_2 : \vert J, K\rangle \to \vert J-1, K-1\rangle \tag{9}$$

From (1)-(3) it is possible to obtain the values for J and K:

$$J = \mathrm{int}\left(\frac{\nu_2 - \nu_1}{2B_v}\right) \tag{10}$$

$$K = \mathrm{int}\left(\frac{1}{2} + \frac{\nu_1 \pm d}{2(A-B)_v}\right) \tag{11}$$

In (10) and (11) by int(x) we mean the integer value closest to x, and d is an average value of d_u and d_l. If the argument of the function int() in (10) and (11) is almost equidistant from two consecutive integers this assignment procedure is not reliable.

In Table 3 we report the calculated J and K values for the investigated pairs. Of course, these assignments rely on the constance of the B_v and d values, which might not be respected if levels not belonging to the first excited amino-wagging, ground torsional state are involved.

4   Conclusion

We observed 24 new FIR laser emissions of hydrazine. These new laser emissions either form pairs sharing the same pump line, or complete such pairs with hydrazine FIR laser emissions already known from the literature. In the latter case, we have measured the relative polarization and pump offset of the partner lines whenever they were not reported in the literature. The availability of laser systems with two emission lines orthogonally polarized and sharing the same upper level is expected to facilitate the determination of the involved J and K quantum numbers, and thus the assignment work. We present complete assignments for four FIR laser emissions, and we propose J and K values for 12 further laser systems.

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