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New Far-Infrared Laser Frequencies Generated by CH3CN, CD3CN, 13CH3I, CD3I, and 13CD3I

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New Far-Infrared Laser Frequencies Generated by CH_3CN, CD_3CN, $^{13}CH_3I$, CD_3I, and $^{13}CD_3I$

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Abstract
Heterodyne techniques have been used to experimentally determine, for the first time, the frequencies for nineteen laser emissions ranging from 264 to 984 GHz. These laser emissions were generated by optically pumping either CH_3CN, CD_3CN, $^{13}CH_3I$, CD_3I, or $^{13}CD_3I$ with a CO_2 laser. This includes the newly discovered 566.325-μm laser emission from optically pumped $^{13}CD_3I$. The fractional uncertainties with which these frequencies were experimentally determined, up to $\pm\, 5 \times 10^{-7}$, were of sufficient accuracy to confirm or revise seven previously proposed far-infrared laser assignments.

Keywords Optically pumped molecular laser · CH_3CN · CH_3I · Isotoplogues

1 Introduction

Direct discharge and optically pumped molecular lasers are capable of generating thousands of laser emissions in the far-infrared region [1–3]. The radiation from these sources have been used to investigate a variety of stable molecules and short-lived free radicals throughout this region of the electromagnetic spectrum.

Recently, we constructed an optically pumped molecular laser system that utilized a transverse, or "zig-zag," excitation scheme [4]. Although this pumping scheme has been used previously [5–8], our experimental system has successfully generated over 600 laser emissions of which 130 were discovered in our lab. Given the wealth of far-infrared laser emissions this system has been capable of generating, we have focused recent efforts in experimentally determining the frequency for any far-infrared laser

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emission we observed. To date, we have experimentally determined over 170 far-infrared laser frequencies with this system. Our current work extends these efforts, in which we have experimentally determined for the first time the frequencies of nineteen far-infrared laser emissions belonging to either optically pumped CH_3CN, CD_3CN, $^{13}CH_3I$, CD_3I, or $^{13}CD_3I$. Included in the present investigation is the discovery of a laser emission from $^{13}CD_3I$, the confirmation of proposed spectroscopic assignments for six far-infrared laser emissions, and the revision of a previously proposed spectroscopic assignment for CD_3I.

2 Experimental Methods

In this investigation, far-infrared radiation is generated using an optically pumped molecular laser system. This system uses a CO_2 pump laser to excite the low pressure far-infrared sample housed in a second laser cavity (i.e., the FIR laser cavity). The far-infrared medium is excited by the CO_2 pump laser's infrared radiation using a transverse, or "zig-zag," pumping scheme [4, 9]. Once far-infrared laser radiation is detected, its frequency is determined using the three-laser heterodyne technique,

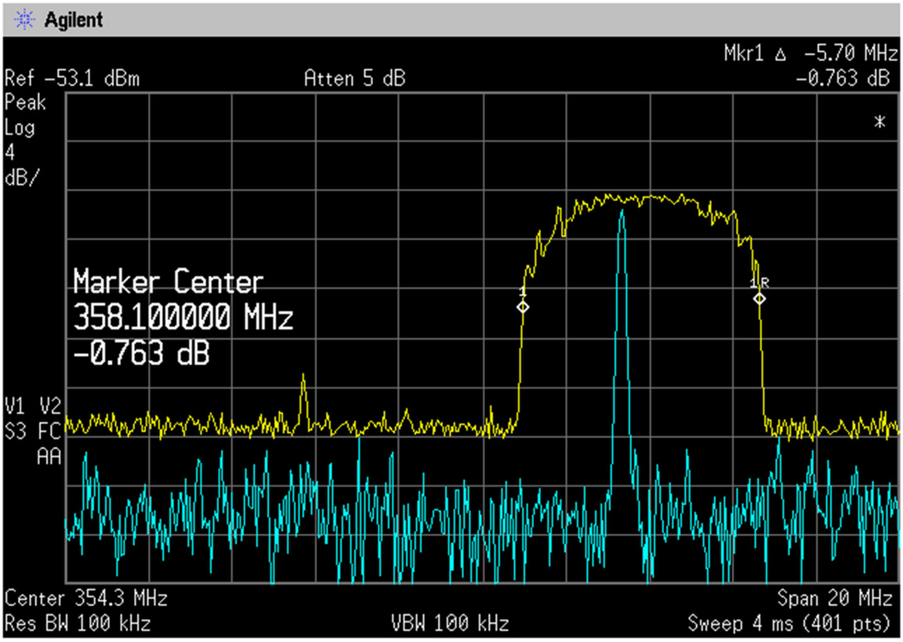

Fig. 1 The lower trace on the spectrum analyzer display is the instantaneous beat observed when the 566.325-μm laser emission is mixed with the stabilized $9P06$ and $9P26$ CO_2 reference laser emissions. Once the instantaneous beat is observed, the far-infrared laser cavity is manually scanned across its gain curve by adjusting the position of one of the far-infrared laser cavity's end mirrors using a micrometer dial. The upper trace, whose center is 358.10 MHz, is the maximum heterodyne signal recorded by the spectrum analyzer during this process

discussed in detail in Refs. [9–11]. Briefly, the far-infrared laser emission is mixed with radiation from two stabilized CO_2 reference lasers with frequencies $\nu_{CO_2(I)}$ and $\nu_{CO_2(II)}$. The difference between these reference laser frequencies and the unknown far-infrared laser frequency is observed on a spectrum analyzer and the beat frequency is subsequently measured, ν_{beat}, an example of which is shown in Fig. 1. The unknown far-infrared laser frequency, ν_{FIR}, is then calculated using

$$\nu_{FIR} = |\nu_{CO_2(I)} - \nu_{CO_2(II)}| \pm \nu_{beat}. \tag{1}$$

To experimentally determine the $\pm$ sign in Eq. 1, the far-infrared laser cavity is manually scanned across its gain curve by translating one of the far-infrared laser cavity's end mirrors using a micrometer dial. A small shift in the beat frequency is subsequently observed on the spectrum analyzer that identifies the appropriate sign to use in this expression.

At least fourteen independent measurements of the beat frequency have been used to calculate each far-infrared laser frequency. Additionally, at least two distinct sets of CO_2 reference laser lines were used to measure the beat frequency for each far-infrared laser emission. The experimental uncertainty reported in this work is derived from the precision of the measured beat frequencies, the symmetry and width of the broadened gain curve of the far-infrared laser, and the overall reproducibility of known frequencies with this system. The resulting one-sigma fractional uncertainty, $\Delta\nu/\nu$, is at least $\pm$ 5 $\times$ 10^{-7}. All samples were commercially obtained with the following enrichments: $\geq$ 99.8% D for CD_3CN, 99% ^{13}C for $^{13}CH_3I$, $\geq$ 99.5% D for CD_3I, and 99% ^{13}C and 99.5% D for $^{13}CD_3I$.

3 Results

The far-infrared laser frequencies determined during this investigation are listed in Table 1. The laser emissions are arranged, by molecule, in order of the CO_2 pump line by increasing wavelength. The corresponding wavelength and wavenumber were calculated for each far-infrared laser frequency using 1 cm^{-1} = 29 979.2458 MHz. During this investigation, the frequencies for known laser emissions (e.g., the 788.481-μm line for $^{13}CD_3I$ generated by 10P12 [12, 13]) were periodically measured and found to be in agreement with their published values.

4 Discussion

During this investigation, one far-infrared laser emission was discovered: the 566.325-μm line generated by $^{13}CD_3I$ when pumped with the 10P46 CO_2 laser emission. This 566.325-μm line was observed to be parallel to the polarization of the CO_2 pump laser radiation and have an optimal operating pressure of 13.3 Pa with an output power characterized as Very Weak (below 1 μW of power). In comparison, the 554.336-μm line was also observed using the 10P46 CO_2 laser emission operating at the same offset frequency and with the same polarization. Although it also

Table 1 New far-infrared laser frequencies generated by optically pumped CH_3CN, CD_3CN, $^{13}CH_3I$, CD_3I, and $^{13}CD_3I$

CO_2 pump	Wavelength (μm)	Frequency (MHz)	Wavenumber (cm^{-1})	Reference
CH_3CN				
9*R*16	441.178	679 526.6 ± 0.4	22.6666	[14]
CD_3CN				
9*R*24	304.468	984 642.7 ± 0.6	32.8441	[15]
9*R*04	329.863	908 838.1 ± 0.5	30.3156	[15]
$^{13}CH_3I$				
10*P*26	543.078	552 024.6 ± 0.4	18.4136	[12, 14, 16]
10*P*30	354.315	846 118.2 ± 0.5	28.2235	[17]
CD_3I				
10*R*02	658.112	455 534.0 ± 0.4	15.1950	[17]
10*P*04	1 135.051	264 122.5 ± 0.3	8.8102	[17]
10*P*08	740.018	405 115.1 ± 0.3	13.5132	[12, 18, 19]
$^{13}CD_3I$				
9*P*36	462.319	648 453.2 ± 0.4	21.6301	[13]
10*P*02	421.033	712 039.5 ± 0.4	23.7511	[20]
10*P*08	606.642	494 183.5 ± 0.7	16.4842	[13]
10*P*14	468.796	639 494.1 ± 0.4	21.3312	[13]
	477.843	627 386.3 ± 0.4	20.9274	[20]
10*P*18	549.425	545 647.2 ± 0.5	18.2008	[13]
10*P*26	813.463	368 538.6 ± 0.5	12.2931	[13]
10*P*46	554.336	540 813.6 ± 0.3	18.0396	[13]
	566.325	529 364.4 ± 0.3	17.6577	New
10*P*48	567.416	528 346.8 ± 0.4	17.6238	[13]
10*P*52	435.777	687 949.1 ± 0.4	22.9475	[13]

used an operating pressure of 13.3 Pa, its output power was characterized as Strong (between 0.1 and 1 mW of power).

Microwave and infrared data can be combined with experimentally determined laser frequencies to perform the spectroscopic assignment of far-infrared laser transitions. Table 2 outlines the assignments associated with seven laser transitions.

Chang and Bridges [14] first observed the CH_3CN 441.178-μm laser emission that was subsequently assigned by Arimondo and Inguscio [21] to be the ground state transition from $J_K = 37_6 \rightarrow 36_6$. Sarkkinen and co-workers [22] reaffirmed their assignment and calculated the laser frequency to be 22.66509 cm^{-1}. Although the experimentally determined laser frequency (22.6666 cm^{-1}) has been significantly improved by this investigation, it still differs from the calculated value by approximately 45 MHz, which is larger than expected. To determine our laser frequency, beat frequencies generated by three distinct sets of CO_2 reference lasers (9*R*22 &

Table 2 Spectroscopic assignments for far-infrared laser emissions

CO_2 pump	Experimental freq. (cm^{-1})	Calculated freq. (cm^{-1})	FIR laser transition $J'_{K'} \rightarrow J''_{K''}$	Reference
CH_3CN				
$9R16$	22.6666	22.66509	$37_6 \rightarrow 36_6$	[21, 22]
CD_3CN				
$9R24$	32.8441	32.84363	$63_1 \rightarrow 62_1$	[15, 22]
$9R04$	30.3156	30.31565	$58_1 \rightarrow 57_1$	[15, 22]
$^{13}CH_3I$				
$10P26$	18.4136	18.41355	$39_6 \rightarrow 38_6$	[16, 18]
$10P30$	28.2235	28.22343	$60_8 \rightarrow 59_8$	[17]
CD_3I				
$10R02$	15.1950	15.19496	$38_6 \rightarrow 37_6$	[17]
$10P04$	8.8102	8.81016	$22_4 \rightarrow 21_4$	[17]

$9P08$, $9R04$ & $9P22$, $9P02$ & $9P28$) were used and there was no discernible variation among the measurements used to calculate this laser frequency. Although the author is unable to explain the larger than expected difference between the calculated and experimentally determined far-infrared laser frequency, the proposed transition remains as originally assigned.

For CD_3CN, these lines were first observed by Gastaud, Redon, and Fourrier [15] in which they proposed the assignments: $J_K = 62_6 \rightarrow 61_6$ (for 304.468 μm) and $J_K = 58_4 \rightarrow 57_4$ (for 329.863 μm). Sarkkinen and co-workers [22] revised these transition assignments and their calculated frequencies, which are in agreement (to within 15 MHz and 2 MHz, respectively) with our experimental results.

While studying CH_3I, Dyubko and co-workers [12] discovered the 543.078-μm laser emission, generated using the $10P26$ CO_2 pump. This laser emission was later confirmed to belong to $^{13}CH_3I$ instead of its parent sample due to its natural abundance. Arimondo et al. [16] initially proposed the IR assignment that was later expanded to include the far-infrared laser transition [18]. Gastaud and co-workers [17] also investigated $^{13}CH_3I$ and were responsible for the discovery, and subsequent assignment, of the 354.315 μm laser emission. Using the molecular constants derived by Alanko [23], the transition assignments and calculated frequencies for both $^{13}CH_3I$ laser emissions are found to be in excellent agreement (to within 1 MHz) with our experimental results.

Finally, for CD_3I, Gastaud and co-workers proposed assignments for the 1 135.051- and 658.112-μm laser emissions [17]. Using an updated set of molecular constants for CD_3I [24], the calculated frequencies for both laser emissions are in excellent agreement (to within 1 MHz) with our experimental results. To accomplish this, a minor adjustment (modifying K from 7 to 6) was made to the assignment of the 658.112-μm laser emission.

5 Conclusion

This work reports the first experimental determination of nineteen far-infrared laser frequencies generated by optically pumped CH_3CN, CD_3CN, $^{13}CH_3I$, CD_3I, and $^{13}CD_3I$. One of these frequencies belong to a newly discovered laser emission from $^{13}CD_3I$, six were used to confirm the proposed spectroscopic assignments of far-infrared laser emissions, and another was used to revise a previously proposed spectroscopic assignment for a laser emission generated by CD_3I. Along with learning more about the laser medium itself, these frequencies can be used to conduct high-resolution spectroscopic investigations in the far-infrared region (e.g., laser magnetic resonance spectroscopy [25]).

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Data Availability The data is available upon request from the corresponding author.

Declarations

Competing Interests The author declares no competing interests.

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