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Heterodyne of Optically Pumped fir Molecular Lasers and Direct Frequency Measurement of New Lines

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Abstract. Direct frequency measurements of optically pumped far infrared (fir) molecular lasers are reported, also for new lines. This heterodyne technique is versatile and simple. By controlling some parameters of resonator and pump source, possible causes of error are evidenced in the precise frequency determination. The implications for molecular spectroscopy are also discussed.

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Optically pumped molecular lasers are the most widely used sources in the fir region of the electromagnetic spectrum. More than two thousand known laser lines span the wavelength spectrum between 20 µm to 2.9 mm (15 THz–100 GHz), with cw power output from less than 0.1 to more than 100 mW, depending on the line and experimental conditions. The absence of a plasma in the cavity, with its inherent fluctuations in the index of refraction is responsible at least in part for linewidths which are narrower than 1 kHz. Also for a conventional laboratory apparatus in free running operation, the uncertainty in the frequency reproducibility if of the order of few parts in 10^7. At frequencies higher than 1 THz, sources of comparable spectral purity and power are not available. As a consequence optically pumped fir lasers have wide application in several fields of physics and in particular in fields for which a precise knowledge of the laser frequency is requested.

For instance, the frequency of the laser output plays also an important role in the spectroscopy of the active molecule itself. Wavelength determinations are limited to a maximum relative accuracy of 10^{-2}–10^{-4} by using either an external interferometer or the laser resonator itself as an interferometer. As a consequence the maximum expected accuracy (a few parts in 10^7) can be reached only by direct frequency measurements. So far the direct frequency measurements have been performed synthetizing a frequency within a radiofrequency difference either from harmonics of frequency stabilized millimeter klystrons or from difference frequencies between two stabilized CO_2 laser lines and possibly an additional microwave oscillator.

Hundreds of fir laser frequencies have been measured [1], providing a comb of reference lines with a medium spacing in the tuning range of microwave oscillators.

This allows now the generalization of the technique reported in [2], where one fir laser emission was measured by beating with a HCN laser whose frequency is by accident close, using instead optically pumped fir laser also for reference.

1. Experimental Apparatus

A general scheme of the experiment is illustrated in Fig. 1. Essentially three independent optically pumped laser systems have been developed.

As for fir resonators we have used two waveguide structures, previously described [3]. We have also used an open structure nearly confocal Fabry-Perot resonator 100 cm long, where high order transverse modes could be controlled by an intracavity iris. The CO_2 pump power was coupled into the resonator through a 1 mm i.d. hole in one gold coated copper end mirror (115 cm radius of curvature). Fir power was coupled out using a variable coupler consisting of an elliptical mirror formed by cutting and polishing a

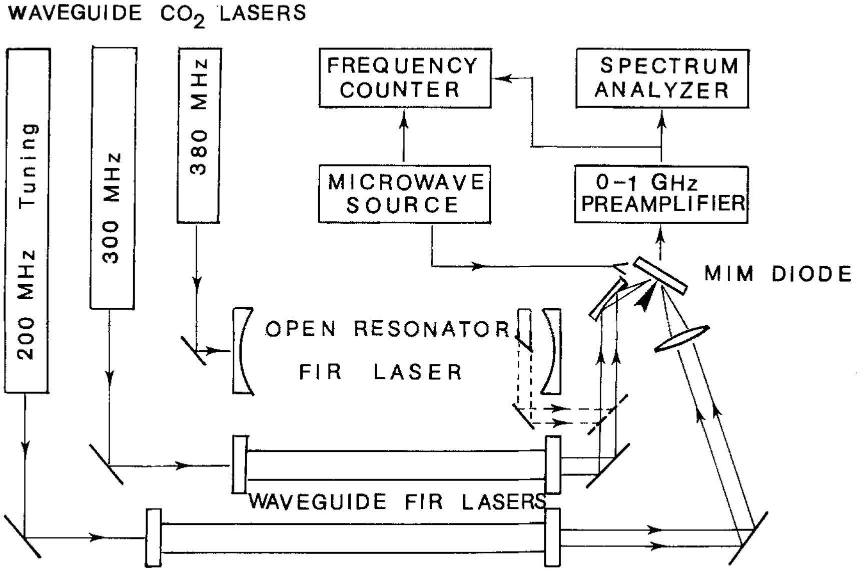

Fig. 1. Scheme of the experimental apparatus used to measure the frequency of optically pumped fir lasers. Point contact MIM diodes are used for non linear mixing. When necessary also tunable microwave radiation is coupled to reduce the beat frequency to the preamplifier bandwidth

6 mm diameter copper cylinder at 45°. The mirror was moved perpendicular to the cavity axis to optimize the output coupling at each wavelength.

As pump sources we used home made [4] high pressure cw waveguide CO_2 lasers. Three independent resonators allowed frequency tunabilities of ± 100, ± 150, and ± 190 MHz around the lines centers. For the frequency measurements two independent CO_2-fir lasers systems were used. The apparatus was very versatile. For each measurement the proper CO_2 and fir resonator were chosen, depending on the particular requirements (power, pump offset, etc.). The two fir outputs were focused on a conical MIM (metal-insulator-metal) W–Ni point contact diode using lenses or parabolic mirrors [5]. The impedance of the diode was mechanically adjusted at about 300–500 Ω, for the maximum speed response [5]. After amplification in a 1200 MHz bandwidth amplifier, the beat note with signal-to-noise (S/N) ratios up to 50 dB could be observed on a spectrum analyzer.

When the frequency difference between the two fir laser lines was larger than the preamplifier bandwidth, microwave power from a sweeper was also coupled on the diode to lower the heterodyne frequency. The frequency of the beat note on the spectrum analyzer and of the sweeper were measured by a frequency counter. The unknown frequency f_x was hence given by

$$f_x = m \cdot f_R \pm n \cdot f_b \pm p \cdot f_{RF}, \qquad (1)$$

where f_R is the frequency of the laser used as reference, f_b and f_{RF} are the frequencies of the beat note and of the microwave. In general m, n, and p can be positive integers larger than one to account for harmonics generation in the diode.

2. Experimental Results

In order to test the accuracy of the technique we have chosen two CH_3OH laser lines at about 232 μm, whose frequency was already known [6]. One emission is pumped by the CO_2 9R(22) line and has a frequency of 1,287,832.2 MHz, the other is pumped by the CO_2 9R(10) line and has a frequency of 1,286,999.5 MHz, hence 832.7 (4) MHz lower than the other. In the experiment we have observed a beating note with a signal-to-noise ratio of about 50 dB at a frequency of 832.5 (5) MHz, in good agreement with the predicted value.

By setting one of the fir cavities fixed and scanning the other, the beat note was observed to change in a range of about 10 MHz. The accuracy of the measurement is affected by the uncertainty in setting both the fir lasers at the center frequency, which introduces a factor $\sqrt{2}$ with respect to systems where only one laser must be resetted. Of course, for the final accuracy also the error in the frequency value of the reference laser must be added. Looking for possible systematic frequency shifts, we kept both the fir cavities fixed approximately at the center of the gain curve and changed the pump frequency. The experimental results reported in Fig. 2 show no observable effects in the beat frequency. These measurements can be added to those recently performed changing pressure of operation [7] to state the frequency reproducibility of free running optically pumped fir lasers in about $\pm 2 \times 10^{-7}$. A three wave mixing could be easily observed by adding a rf field. This encouraged measurements for which the frequency difference between the two fir lasers was higher than the preamplifier bandwidth. An example is given by frequency measurement of the CH_3OH laser line pumped by the CO_2 9R(10) with large offset and

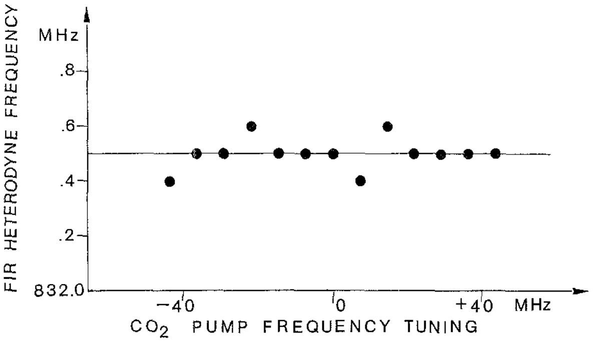

Fig. 2. Dependence of the heterodyne beat frequency as a function of the CO_2 pump lasers detuning

reported in the literature [8] at a wavelength of 190.6(1) μm, corresponding to 1,572.5 GHz. As reference laser we used the CH_3OH emission at 1,564,518.7 MHz, $10R(10)$ pumped. We coupled on the diode also radiation from a microwave sweeper and observed the three-wave beat note for $f_{RF} = 14$ GHz. Typical spectrum analyzer recordings are shown in Fig. 3. In a) the fir cavity was scanned to search for well symmetric tuning curves, essential for a precise and unambiguous determination of the line centers. In b) the beat note, only a few hundred kilohertzs broad, is recorded with both the fir cavities fixed at the center of the tuning curves. It is worth noting that for these measurements one of the two lasers was operated by pumping in long-pulse regime.

In the measurements in Fig. 3 it was $f_b = 6$ MHz and $f_{RF} = 13{,}814.7$ MHz yielding, from (1), $f_x = 1{,}578{,}339.4$ (10) MHz. The heterodyne signal was observed also for $f_{RF} = 6910.1$ MHz, and in this case from (1) with $p = 2$ we obtained $f_x = 1{,}578{,}338.9$ (10) MHz. In Table 1 the average between the two values has been reported. Of course, two completely different active gases could be used in the two fir resonators. This is the case of the CH_2F_2 new emission pumped at large offset with the $9R(14)$ CO_2 line [9]. From the measurement of the wavelength we had $\lambda = 337.97$ (20) μm corresponding to $\nu = 887.04$ (50) GHz. As reference for the direct frequency measurement we used the $^{13}CH_3OH$ ($9P22$ pump) emission at 884,438.0 MHz. We observed the heterodyne signal for $f_{RF} = 3113.1$ MHz yielding $f_x = 887{,}551.1$ (15) MHz, as reported in Table 1. The measurements on this laser line have been performed also using the confocal resonator for the reference laser. The importance of the iris placed inside the cavity is demonstrated by the measurements shown in Fig. 4. In a) the beat note on the spectrum analyzer, recorded as a function of the confocal cavity length, is recorded with the iris broadly opened. Different structures are evident, possibly given by lasing on transverse modes which are mixed also because of our asymmetric outcoupling geometry. This feature can cause mistakes in the determination of the center frequency of lasing. The importance of the use of the intracavity iris is shown in b). Here a clear and

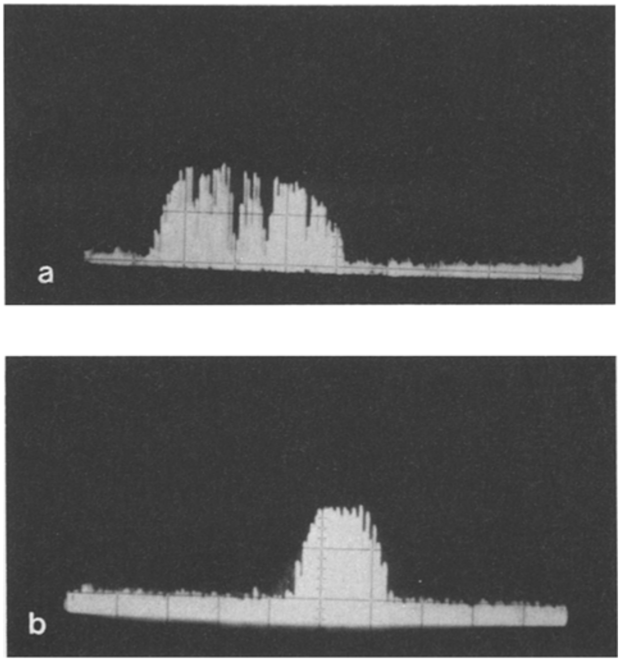

Fig. 3a and b. Spectrum analyzer recording of the heterodyne signal from two CH_3OH lasers ($9R10$ and $10R10$ pumps) and a microwave radiation. The waveguide configuration was used for both the fir resonators. In (a) the length of one of the two fir resonators was scanned and a symmetric frequency tuning curve was displayed (horizontal 0.5 MHz/div; vertical 10 dB/div). In (b) both the resonator lengths were kept constant. Long-pulsed operation was used for one of the lasers (horizontal scale 0.2 MHz/div; vertical 10 dB/div)

Table 1. New frequency measurement

Lasing molecule	CO_2 pump	Assignement	Frequency [MHz]
CH_3OH	$9R(10)$	$(n\tau K, J): (013, 28) \rightarrow (022, 27)$	1,578,339.2 (15)
CH_2F_2	$9R(14)$	$(J, K): (23, 12) \rightarrow (23, 11)$	887,551.1 (15)
CH_3F	$9P(20)$	$(J, K): (12, 1) \rightarrow (11, 1)$	604,334.7 (10)
CH_3F	$9P(20)$	$(J, K): (12, 3) \rightarrow (11, 3)$	604,236.9 (15)

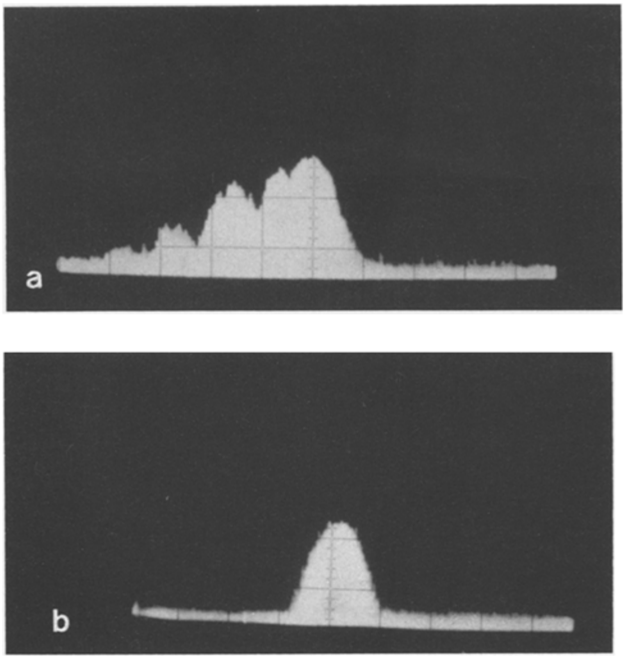

Fig. 4a and b. Spectrum analyzer recording of the heterodyne signal from a CH_2F_2 laser (9*R*14 pump), a $^{13}CH_3OH$ reference laser (9*P*22 pump) and a microwave radiation. For the $^{13}CH_3OH$ laser the nearly confocal resonator was used. In (a) the intracavity iris was fully opened, while in (b) it was reduced in order to obtain lasing action only on the higher gain mode

symmetric tuning curve survives. By a comparison between a) and b) it is also evident a sort of pulling effect of other structures on the principal one.

The new frequency measurements so far reported are for new laser emissions pumped thanks to the larger tunability of high pressure waveguide CO_2 lasers used as pump sources. In the following we shall further illustrate this interesting feature using the fir emission at 496 µm from CH_3F. Using a conventional cw CO_2 laser the 9*P*(20) emission can be resonant with the CH_3F ν_3, $Q_{12,2}$ vibrational transition (offset +40.1 MHz) and the $Q_{12,1}$ (−58.6 MHz). The tunability of our CO_2 laser (380 MHz) allows also the cw pumping of the $Q_{12,3}$ (+207.9 MHz) component.

A typical optoacoustic recording of the CH_3F absorption around the 9*P*(20) emission is shown in Fig. 5. The $K=1$ component is well in resonance and cw fir emission can be easily obtained. The center of the $K=3$ component is not exactly in the CO_2 tuning range. On the other hand, the $K=3$ absorption is very strong due to the degeneracy in CH_3F, and enough molecules are pumped in the Doppler profile. In fact in b) it is shown the fir laser emission corresponding to $K=3$ component pumping.

Using our heterodyne apparatus both $K=1$ and $K=3$ fir emissions can be measured by beating with a reference laser working on the $K=2$ emission. The

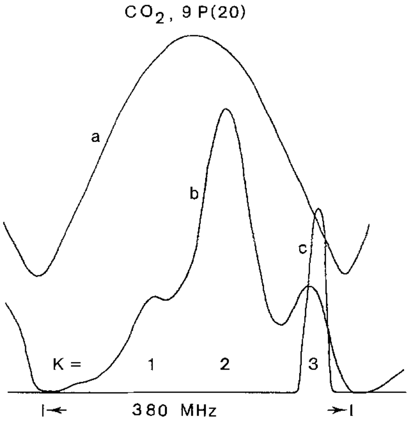

Fig. 5a–c. Optoacoustic recording of the CH_3F absorption around the CO_2 9*P*(20) line. (a) CO_2 laser pump power. (b) The three different peaks correspond to the components of the ν_3, Q_{12} transition with $K=1, 2, 3$. In (c) the fir emission corresponding to $K=3$ is recorded

frequency is well known since it has been measured independently in several laboratories with results in agreement within a few hundred kHz.

Our present results for $K=1$ and $K=3$ component emissions are reported in Table 1. As for $K=3$, the measurement was performed using the waveguide fir resonator for the $K=2$ reference laser. The low threshold open structure resonator was used for the $K=3$ emission. A typical spectrum analyzer recording of the heterodyne signal is shown in Fig. 6. The measurement was performed by keeping fixed the reference laser cavity and scanning the open structure cavity length. Differently from all other measurements, in this case we were not able to obtain a symmetric tuning curve. This possibly could be caused by the large detuned pumping of the $K=3$ component. For this reason the error quoted for this measurement is larger than for the others.

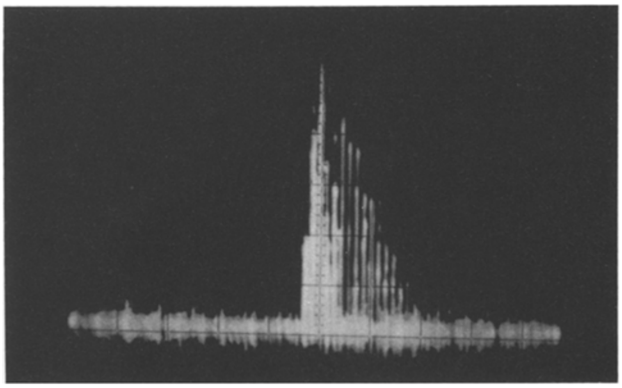

Fig. 6. Spectrum analyzer recording of the heterodyne signal between a CH_3F ν_3, $J=12-11$, $K=2$ and a CH_3F ν_3, $J=12-11$, $K=3$ laser. The beat note is at 60.5 (15) MHz. The horizontal scale is 1 MHz/div and the vertical 10 dB/div

3. Relevance for Molecular Spectroscopy

As discussed in the introduction, the direct measurement of the frequency of fir optically pumped lasers is important also for the spectroscopy of the active molecule itself. In the following we shall illustrate this feature for the fir molecular transitions measured in the present paper.

3.1. CH_3OH

The measured line had been reported in [8] with an energy of 52.45 (3) cm^{-1} from the wavelength measurements. Precise numbers are available for the infrared transitions and other coupled fir absorptions [10]. Also, precise microwave values have been obtained for the K asymmetry splitting of some of the involved levels by means of triple resonance experiments [11], unambiguously confirming the ir-fir transition assignments. From a loop of all these data it was possible to extrapolate from a loop-computation an energy of 52.637 cm^{-1} for the new line. The precise experimental data from the measurement of Table 1 is 52.64773 (5) cm^{-1}. This confirms the reliability of the loop computation to a level of few MHz and the limited usefulness of wavelength measurements for higher accuracy molecular spectroscopy purposes.

3.2. CH_2F_2

The new frequency measured line has been assigned in [9]. The energy separation as deduced from the frequency measurement is 29.60552 (5) cm^{-1}, while the calculated value from the existing molecular parameters is 29.819. The present measurements in this case suggest the possibility of including CH_2F_2 fir frequency measurements in a general fit of the data available for the molecule and improving the molecular parameters knowledge.

3.3. CH_3F

This molecule has played a key role in the development of molecular spectroscopy. Several high precision measurements have been reported and accurate sets of rotovibrational constants are available for the molecule [12]. It is hence possible to compute for the difference between the ν_3, $J=12$, K transitions:

$$\Delta_{1-2} = 37.072\,(60)\,\mathrm{MHz},$$

$$\Delta_{2-3} = 61.885\,(100)\,\mathrm{MHz}.$$

Our experimental results give: $\Delta_{1-2} = 37.3\,(10)$ MHz and $\Delta_{2-3} = 60.5\,(15)$ MHz.

Note the large deviation from the accurate computed value, caused by the large pump offset, combined with very high fir gain.

4. Conclusion

The technique so far illustrated can be applied all widely the far-infrared spectrum, provided that a reference laser line is available and possibly adding tunable microwave radiation to the heterodyne.

This second generation technique is simpler than the original ones critically reviewed in [1].

The frequency values obtained for new lines have been used for a spectroscopical analysis of the lasing molecules.

The accurate measurements have evidenced the necessity of a careful design and control of resonator parameters to avoid shifts for instance induced by competitive modes.

Note added in proof: Recently F. De Lucia and D. Skatrud (private communication) have performed high accuracy measurements in the $\nu=3$ state of CH_3F by means of tunable absorption spectroscopy. They obtain:

$$\nu(12,1)\rightarrow(11,1) = 604{,}334.395\,(50)\,\mathrm{MHz},$$

$$\nu(12,3)\rightarrow(11,3) = 604{,}235.623\,(50)\,\mathrm{MHz}.$$

Both the values agree with those reported in Table 1, thus giving also a good confirmation of the correct evaluation of the errors in our work.

References

1. M. Inguscio, G. Moruzzi, K.M. Evenson, D.A. Jennings: Rev. Appl. Phys. 1986 (in press)
2. P.S. Epton, W.L. F.K. Tittel, T.A. Robson: Appl. Opt. **18**, 1704–5 (1979)
3. F. Strumia, M. Inguscio: Stark Spectroscopy and Frequency Tuning in Optically Pumped Far-Infrared Molecular Lasers. In: *Infrared and Millimeter Waves* **3**, 129–213 (Academic, New York 1982)
4. N. Ioli, V. Panchenko, M. Pellegrino, F. Strumia: Appl. Phys. B **38**, 23–30 (1985)
   F. Strumia, N. Ioli: High Power C.W. Waveguide CO_2 Lasers. In: *Physics of New Laser Sources*, ed. by N.B. Abraham, F.T. Arecchi, A. Mooradian, A. Sona (Plenum, New York 1985) pp. 189–199
5. K.M. Evenson, M. Inguscio, D.A. Jennings: J. Appl. Phys. **56**, 956–960 (1985)
6. F.R. Petersen, K.M. Evenson, D.A. Jennings, A. Scalabrin: IEEE J. QE-**16**, 319–323 (1980)
7. M. Inguscio, K.M. Evenson: Opt. Lett. **9**, 443–444 (1984)
8. J.O. Henningsen, M. Inguscio, A. Moretti, F. Strumia: IEEE J. QE-**18**, 1004–1008 (1982)
9. N. Ioli, A. Moretti, G. Moruzzi, F. Strumia, F. D'Amato: Int. J. IR mm waves **6**, 1017–29 (1985)
10. G. Moruzzi, F. Strumia, F. Colao: Infr. Phys. **25**, 251 (1985)
11. N. Ioli, A. Moretti, F. Strumia, I. Longo: Opt. Lett. **10**, 330 (1985)
    N. Ioli, A. Moretti, G. Moruzzi, P. Roselli, F. Strumia: In: *Laser Spectroscopy*, VII, ed. by Y.R. Shen, T.W. Hänsch, Springer Ser. Opt. Sci. **49** (Springer, Berlin, Heidelberg 1985) pp. 49–50
12. E. Arimondo, M.I. Schisano, P.B. Davies, P.A. Hamilton: Infr. Phys. **25**, 209–213 (1985) and references therein

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