Heterodyne Measurements of Submillimeter Laser Spectrometer Frequencies

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Abstract—**The frequencies of 46 CW laser lines commonly used for submillimeter spectroscopy, with wavelengths between 0.1 and 0.7 mm, have been measured by heterodyne methods. All the lines are optically pumped by a CO_2 laser, with threshold pump powers of 3 W or less. The precision of measurement, limited by the laser linewidth, is typically ±1 part per million.**

Optically pumped submillimeter lasers are finding increasing use as sources of radiation for magnetic resonance spectroscopy, a technique in which a variable magnetic field is used to shift molecular spectral lines into coincidence with fixed-frequency laser lines. Since the submillimeter laser frequencies are generally self-stable and resettable to within a fraction of a megahertz, knowledge of laser frequencies at this level of precision is useful in the planning and analysis of magnetic resonance measurements. To reach this precision in line frequency measurements, heterodyne detection with a stabilized local oscillator is necessary. We have made such measurements on 46 laser lines in the wavelength range 0.1–0.7 mm, optically pumped by a CW CO_2 laser. Added to previous measurements of water vapor and methanol line frequencies [1], these measurements provide an essentially complete compilation of line frequencies for laser magnetic resonance spectrometers currently in use.

The oscillating frequencies of laboratory lasers of the waveguide type were measured by one of two different heterodyne methods, according to wavelength. For wavelengths longer than 0.2 mm the laser output was focused on a Shottky diode, where it was mixed with harmonics of a phase-locked millimeter-wave klystron. For wavelengths shorter than 0.2 mm the laser output was focused on a tungsten-nickel point-contact diode, and mixed with standard submillimeter frequencies generated from two absorption-stabilized CO_2 lasers [1]. The long-wave methanol laser lines have been measured by both methods, and agreement is found within ±0.5 MHz, the estimated resetting error. Beat frequencies between the unknown laser frequency and the standard frequencies were amplified and measured with a spectrum analyzer or frequency counter.

The results are given in Tables I and II. For completeness,

TABLE I
LASER LINES MEASURED WITH SUBMILLIMETER-WAVE REFERENCE FREQUENCY

Laser Line λ (μm)	Measured Frequency (MHz) (Uncertainty: ± 0.5 MHz)	CO_2 Pump Line (μm)	Polarization [a]	Threshold Pressure (mT) [b]	Threshold Pump Power (W) [b]	$^{12}C^{16}O_2$ Synthesis Combination [c]
CH_3OH						
70.5	4251668.7	P(34), 9.7	⊥	< 20	<< 1	$R_{II}(30) - P_I(22)$
96.5	3105936.8	R(10), 9.3	∥	100	3	$R_{II}(20) - R_I(18)$
118.8	2522781.0	P(36), 9.7	⊥	30	<< 1	$P_{II}(14) - R_I(8)$
163.0	1838839.3	R(38), 10.1	∥	35	< 1	$P_{II}(20) - R_I(36)$
170.6	1757526.3	P(36), 9.7	∥	30	<< 1	$P_{II}(30) - R_I(24)$
232.9	1286999.5	R(10), 9.3	∥	85	< 1	$R_{II}(32) - P_{II}(24)$
251.1	1193727.3	R(38), 10.1	⊥	35	< 1	$R_I(34) - P_I(20)$
392.1	764642.6	P(36), 9.7	⊥	25	3	$R_{II}(6) - P_{II}(24)$
469.0	639184.6	R(38), 10.1	⊥	75	1.5	$P_I(8) - P_I(32)$
570.6	525427.5	P(16), 9.5	∥	60	2.5	$P_{II}(18) - P_{II}(36)$
699.4 [d]	428628.5	P(34), 9.7	⊥			$R_I(38) - R_I(14)$
CH_3OD						
103.1	2907088.9	P(30), 9.6	⊥	50	<< 1	$R_{II}(30) - R_I(40)$
117.2	2557365.4	P(26), 9.6	∥	70	1.5	$R_{II}(10) - R_I(38)$
CH_3NH_2						
147.8	2027752.6	P(24), 9.6	⊥	60	2	$P_{II}(18) - R_I(28)$
N_2H_4						
181.9	1647877.4	P (6), 10.5	∥	60	< 1	$P_{II}(34) - R_I(24)$

[a] Polarization of submillimeter laser output with respect to linearly polarized pumping radiation.
[b] For a Fabry-Perot cavity, axially pumped through a central hole in one mirror.
[c] The subscripts I and II mean 10.5-μm band and 9.5-μm band, respectively.
[d] A low-threshold line, but not yet operated successfully in a laser resonance spectrometer.

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TABLE II

LASER LINES MEASURED WITH MILLIMETER-WAVE REFERENCE FREQUENCY

Laser Line λ (μm)	Measured Frequency (MHz)	Frequency Uncertainty (MHz)	CO_2 Pump Line (μm)	Polarization[a]	Threshold Pressure (mT)[b]	Threshold Pump Power (w)[b]
HCOOH						
302.3	991777.8	± 1.0	R (4), 9.4	∥	< 20	<< 1
393.6	761606.5	± 0.5	R(18), 9.3	∥	< 20	<< 1
405.6[c]	739161.0	± 0.7	R(18), 9.3	∥		
418.6	716156.4	± 0.5	R(22), 9.3	∥	< 20	<< 1
432.6	692950.5	± 0.5	R(20), 9.3	∥	< 20	<< 1
458.5	653821.4	± 0.5	R(38), 9.2	⊥	30	< 1
513.0	584386.9	± 0.7	R(28), 9.2	∥	< 20	<< 1
669.5[c]	447766.0	± 0.8	R(30), 9.2	∥	20	1
N_2H_4						
192.9	1647877.4	± 3.0	P(24),10.6	⊥	50	< 1
233.9	1281625.8	± 1.0	R(8),10.3	∥	30	<< 1
264.8	1132140.6	± 1.0	R(20),10.2	∥	50	< 1
301.3	995077.8	± 1.5	R(12),10.3	∥	40	1.5
311.1	963731.4	± 1.0	P(20), 9.6	∥	30	1.5
331.7	903889.4	± 1.0	P(12), 9.5	⊥	50	2
435.8	687957.4	± 0.5	P(24),10.6	⊥	50	2.5
461.1[c]	650207.7	± 1.0	P(16),10.6	⊥		
527.9	567925.4	± 1.0	P(12), 9.5		50	1
CH_3F						
496.1	604297.1	± 0.5	P(20), 9.6	⊥	< 20	< 1
CH_3I						
447.1	670462.4	± 0.5	P(18),10.6	∥	60	1
CH_3NH_2						
314.8	952185.0	± 1.5	R (4), 9.4		40	1.5
CH_3CN						
453.4	661213.4	± 1.0	R(16), 9.3	⊥	< 20	3
494.6	606074.7	± 1.0	P (6), 9.4		< 20	< 1
CH_3CH_2F						
405.5	739307.5	± 1.0	R(30), 9.2		20	< 1
502.3	596884.2	± 1.0	R(24), 9.2		20	1
519.1	577551.1	± 1.5	R (4), 9.4		20	3
593.5	505121.4	± 1.0	P(36), 9.7		20	1.5
CH_2CHCl						
385.9	776847.1	± 1.0	P(22),10.6	⊥	30	1.5
442.2	678006.1	± 1.0	P(16),10.6		15	< 1
507.6	590626.3	± 1.0	P(22),10.6	⊥	20	2
567.9	527853.9	± 1.0	P(16),10.6		15	< 1
601.9	498079.1	± 1.0	P(38),10.8		20	1.5
634.5	472507.8	± 1.0	P(20),10.6	∥	20	< 1
$C_2H_2F_2$						
375.5	798286.6	± 1.0	P(12),10.5	∥	50	2
407.3	736059.6	± 1.0	P(14),10.5	∥	50	2
554.4[c]	540785.1	± 2.0	P(14),10.5	⊥		
662.8[c]	452301.5	± 1.0	P(24),10.6	∥		

[a]Polarization of submillimeter laser output with respect to linearly polarized pumping radiation.
[b]For a Fabry–Perot cavity, axially pumped through a central hole in one mirror.
[c]A low-threshold line, but not yet operated successfully in a laser resonance spectrometer.

and also to provide the threshold data that are important for experimental spectroscopy, the earlier measurements of low-threshold methanol lines by Peterson *et al.* [1] are reprinted in Table I. The threshold measurements were made on the Fabry-Perot laser magnetic resonance spectrometer described by Wayne and Radford [2]. Pump power was measured with a calorimetric beam probe outside the Fabry-Perot cavity; the efficiency of coupling this power into the cavity was approximately 80 percent. By threshold pressure is meant the optimum gas pressure for pump power levels slightly over threshold. The sensitivity of a laser resonance spectrometer is poor at threshold, but increases rapidly with gas pressure and pump power. For spectrometers currently in use the maximum usable pump power is limited to 3-4 W by the presence of a thin plastic diaphragm in the submillimeter laser cavity.

Recently some of the laser lines of HCOOH, CH_3I, and CH_3F have been measured with heterodyne detectors by Kramer and Weiss [3] and by Dangoisse *et al.* [4]. Their results are generally in good agreement with those in Table II, the worst-case difference being 1.3 MHz.

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