

Spiers Memorial Lecture

Far-infrared Laser Magnetic Resonance\*

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National Bureau of Standards, Boulder, Colorado, U.S.A.

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## Far-infrared Laser Magnetic Resonance\*

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Far-infrared laser magnetic resonance (l.m.r.) is now a laboratory spectroscopic technique used in at least six laboratories throughout the world, and some 50 papers on l.m.r. spectroscopy have been published.<sup>1-50</sup> L.m.r. is an extremely sensitive technique for finding rotational Zeeman spectra in paramagnetic atoms and molecules. Some 31 species have been detected, some of which had never been discovered before. L.m.r. is now also used in a number of laboratories to study the reaction rates of these paramagnetic free radicals.<sup>37</sup> The field of mid-infrared l.m.r. using CO and CO<sub>2</sub> lasers has also expanded rapidly and is summarized in McKellar's paper<sup>51</sup> at this meeting.

A review of far-infrared l.m.r. was presented a little over one year ago.<sup>37</sup> The purpose of the present report is to bring that comprehensive paper up to date and to point out some recent results in the field of laser frequency measurements which are leading the way to a redefinition of the metre.

In this publication, I will list all of the far-infrared l.m.r. spectroscopic papers chronologically;<sup>1-50</sup> give a list of all the species observed with references, describe the design of a new l.m.r. spectrometer in the N.B.S. Boulder Laboratories; present some new ideas on the sensitivity of intracavity absorption; and finally show how recent laser frequency measurements are leading to a new definition of the metre in terms of the second, thus fixing the value of the speed of light.

### FAR-INFRARED PARAMAGNETIC FREE RADICALS

The first 50 entries in the bibliography are a current chronological list of the l.m.r. spectroscopic papers. In table 1 a list of all the far-infrared l.m.r. molecules identified up to now is presented. The far-infrared l.m.r. spectra of 26 different species, 5 metastable electronic states and several vibrationally excited states have been observed. Some of the observed species are not "well-behaved", that is, the spin decouples from the orbital angular momentum at low field, and the l.m.r. spectrum is not observable at fields of more than a few hundredths of a tesla (a few hundred gauss). Species exhibiting this behaviour are: CCH, CH<sub>2</sub>F and CH<sub>2</sub>OH. These weakly coupled molecules contrast with strongly coupled molecules such as OH, where spectra have been observed to 5 T (50 kG).<sup>9</sup> Generally most spectra are observed below 2 T. The rate of new entries may be slower in the future because the "easier" radicals have already been observed.

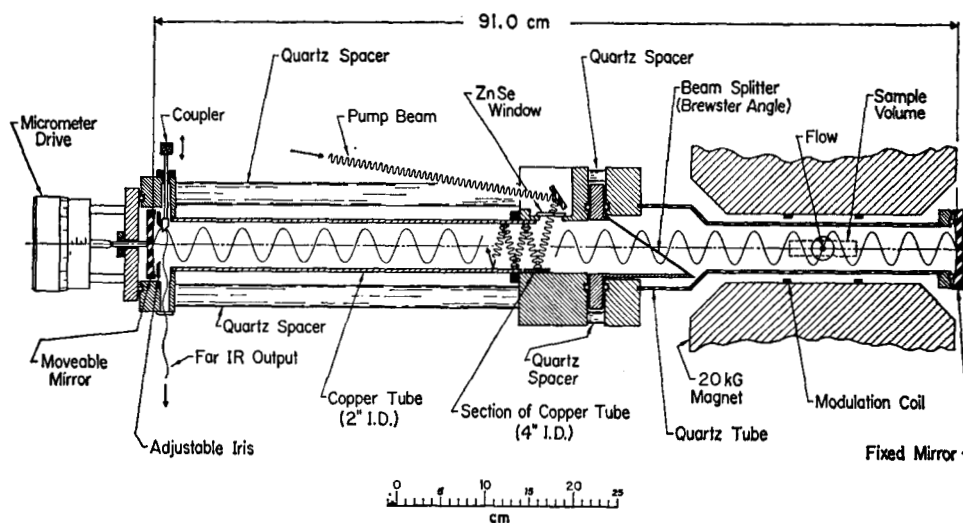
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TABLE 1.—ATOMS AND MOLECULES DETECTED BY FAR-INFRARED LASER MAGNETIC RESONANCE

species	state	reference	species	state	reference
atoms			triatomic		
O	$3p$	28, 34	NO <sub>2</sub>	$^2A_1$	6
C	$3p$	42	HO <sub>2</sub>	$^2A''$	12, 15, 16
			HCO	$^2A'$	17
diatomic			polyatomic		
O <sub>2</sub>	$^3\Sigma^-$	1, 8, 10, 13	PH <sub>2</sub>	$^2B_1$	21, 36
NO	$^2\Pi$	7	NH <sub>2</sub>	$^2B_1$	18
CH	$^2\Pi$	5, 27	CH <sub>2</sub>	$^3B_1$	38
PH	$^3\Sigma^-$	20	CCH	$^2\Sigma^+$	53
NH	$^3\Sigma^-$	19	metastables		
ClO	$^2\Pi$	52	O <sub>2</sub>	$^1\Delta_u$	48
CF	$^2\Pi$	50	PH	$^1\Delta$	20
OH	$^2\Pi$	9, 32, 33,	HO <sub>2</sub>	$^2A'?$	16
	$v = 0, 1, 2, 3 \dots$	47, 49	CO	$a^3\Pi$	54
OD	$^2\Pi$	41, 49	NF	$^1\Delta$	46
	$v = 0, 1, 2, 3 \dots$				
SeH	$^2\Pi$	29			
SeD	$^2\Pi$	44			
SH	$^2\Pi$	30			
ions					
HBr <sup>+</sup>	$^2\Pi$	35			
DBr <sup>+</sup>	$^2\Pi$	35			

## EXPERIMENTAL DETAILS

A new far-i.r. l.m.r. spectrometer has been constructed in our N.B.S. Boulder laboratory which should be more sensitive, allow more lines to lase, and which will be significantly easier to operate. The new spectrometer is shown in fig. 1. A new com-

FIG. 1.—Laser magnetic resonance spectrometer, 40-1000  $\mu\text{m}$ .

puter-controllable 15 in. electromagnet with ring-shimmed Hyperco pole caps produces a 7.5 cm homogeneous field region 5 times longer than that of our previous spectrometer;<sup>37</sup> hence, it should be five times more sensitive. The new f.i.r. cavity is 25 cm shorter and should oscillate to well over 1000  $\mu\text{m}$ . Better overlap between pump and f.i.r. laser yields a lower threshold of oscillation and consequently a larger number of f.i.r. lines. The improved overlap was accomplished with a nearly confocal mirror geometry, the insertion of the  $\text{CO}_2$  pump at the beam waist and the use of a cylindrical copper tube as the  $\text{CO}_2$  reflector. This cylindrical copper tube was found to double the output power in a f.i.r. laser compared with the use of flat side mirrors. A section of 4 in. I.D. copper tube is used as the first cylindrical  $\text{CO}_2$  beam focuser to begin a series of consecutive refocuses of the pump beam. Quartz is used as the spacers in the spectrometer to provide better thermal stability. For ease of operation, the micrometer, coupler, detector,  $\text{CO}_2$  laser grating, and gas-handling system are all available from one side of the magnet. The beam splitter is rotatable about the laser axis so the polarization can be rotated.

#### INTRA-CAVITY SENSITIVITY

Measurements of the sensitivity of our previous intracavity far-infrared l.m.r. spectrometer indicated an enhancement of sensitivity by about a factor of 20 over what one would expect from a passive cavity.<sup>37</sup> Recently, Radford and Rohbeck<sup>55</sup> used a simple expression of Rigrod's<sup>56</sup> for the saturated c.w. gain of a homogeneously broadened laser. The expression may explain the enhanced sensitivity. Rigrod's expression is

$$\text{gain} = \frac{2gL}{1 + P_{\text{in}}/P_s}$$

where  $g$  is the low-signal gain per unit length,  $L$  is the length of the gain cell,  $P_{\text{in}}$  is the power density in the laser cavity, and  $P_s$  is the self-saturation power level. Then, letting

$$\text{gain} = \text{loss}$$

where the loss is given by  $t + a$ , with  $t$  the fractional coupling,  $a$  the round-trip cavity loss,  $P$  the power output of the laser, and

$$P = \frac{tP_{\text{in}}}{2}$$

one obtains:

$$P = \frac{tP_s}{2} \left( \frac{2gL}{t+a} - 1 \right). \quad (1)$$

For an additional small absorption  $\alpha l$ , where  $\alpha$  is the absorption coefficient and  $l$  is absorption length, the signal is given by

$$\Delta P = P(a + 2\alpha l) - P(a);$$

and substituting in eqn (1), one obtains:

$$\Delta P = \frac{tP_s}{2} \left( \frac{2gL}{t+a} \right) \left( \frac{2\alpha l}{t+a} \right). \quad (2)$$

Now, we would like to find  $\Delta P = f(P)$ , so we will eliminate  $g$  between eqn (1) and (2); thus

$$\Delta P = \left( P + \frac{tP_s}{2} \right) \left( \frac{2\alpha l}{t+a} \right). \quad (3)$$

We have found that the maximum sensitivity occurs with the spectrometer oscillating well above threshold, and this expression seems to be in agreement with the experimental results: (i) the sensitivity is nearly independent of  $P$ , *i.e.*  $tP_s/2 > P$ , (ii) the sensitivity is some 20 times more than one would expect from a passive cavity, *i.e.*  $tP_s/2 \approx 20P$ , (iii)  $\Delta P \propto 2al$  (the spectrometer is linear), (iv)  $\Delta P \propto$  cavity  $Q$  [*i.e.*  $\Delta P \propto 1/(t + a)$ ], (v)  $\Delta P \propto$  pressure of lasing gas (*i.e.*  $\Delta P \propto P_s$ ). However, before a positive confirmation can be made, further experimental verification is needed.

#### RADIO ASTRONOMY

Radio-astronomical observations (*i.e.* with heterodyne techniques) have recently been extended well into the far-infrared region.<sup>57,58</sup> These observations are made at high altitudes in the NASA Kuiper Airborne Observatory or from the top of Mauna Kea in Hawaii. Radio-astronomical searches require an accurate knowledge of the frequencies of the atom or molecule sought. This accuracy generally cannot be supplied with optical data, but can be supplied from l.m.r. data. In fact, the discovery of atomic carbon<sup>57</sup> in Orion was made possible from l.m.r. measurements of atomic carbon which yielded the fine-structure separations<sup>42</sup> good to better than 1 MHz and some 100 times more accurate than optical data.

The measurements of the l.m.r. spectrum of OH<sup>47</sup> also yielded improved rotational frequencies of OH and hence more accurate Doppler shifts in the recent astronomical observations of OH.<sup>59</sup> These astronomical measurements were made with interferometric techniques and hence did not require high-accuracy data for the astronomical detection.

The first terrestrial detection of CCH was performed with far-infrared l.m.r.<sup>53</sup> following the radio-astronomical detection of the  $N = 0 \rightarrow 1$  transition.<sup>60</sup> A precise fit of the l.m.r. data has yielded separate values for  $B$  and  $D$  and thus accurate  $N = 2 \rightarrow 3$  transition frequencies.<sup>53</sup> These transitions have just been observed with radio techniques.<sup>61</sup>

With these successes in the last two years it seems likely that the measurement of other free radicals should lead to their detection in interstellar space. In fact, NASA is now supporting our spectroscopy for exactly this purpose.

#### ACCURATE DETERMINATION OF MOLECULAR CONSTANTS FROM L.M.R. DATA

To determine more accurately structural constants of paramagnetic molecules, Brown *et al.*,<sup>47</sup> have fitted all the l.m.r. data of OH to an effective Zeeman Hamiltonian in order to obtain a highly accurate set of rotational constants. With these constants, predictions of the zero-field term values to *ca.* 3 MHz was possible. Although this determination is *ca.* 3 times less accurate than the atomic carbon numbers, it is quite comparable when one considers that the two atomic carbon transitions were determined with 10 different laser frequencies. Thus, we see that the Zeeman theory for diatomics is approximately as accurate as it is for atoms. That is, the uncertainties are mainly caused by uncertainties in the experimental data, notably from measurements of the magnetic field and the laser frequency.

The Zeeman theory of polyatomics is, in general, not as accurate. One of the best examples of a "successful" Zeeman theory of a triatomic is with HO<sub>2</sub>. The abundant and regular l.m.r. spectrum of HO<sub>2</sub> was fitted very nicely to the theory of Hougen.<sup>15</sup> In contrast, CH<sub>2</sub> exhibits sparse and irregular spectra,<sup>38</sup> and the spectra have not yet been assigned. A crucial test of the Zeeman theory of triatomics will

be made in fitting these data to find a set of rotational constants for this elusive molecule.<sup>38</sup> We feel that more l.m.r. data are needed than are now at hand. A few of the lower levels of CH<sub>2</sub> will certainly be of interest to radio astronomers, and work is continuing on this molecule.

One of the recent outstanding achievements in far-infrared l.m.r. spectroscopy and Zeeman theory is the observation of a previously speculated molecule CH<sub>3</sub>O,<sup>24</sup> and the subsequent fit of its l.m.r. spectrum<sup>40</sup> yielding the rotational constants of this polyatomic radical.

The successful fits of l.m.r. data have been to radicals in which the spin remains coupled to the rotation of the molecule. However, the success with fitting the CCH spectrum indicates that some of these too may be amenable to analysis.

#### THE FUTURE OF L.M.R.

Most of the ground states of the more common paramagnetic hydrides have been observed. A few of the more elusive ones such as SiH still elude the experimentalist. However, hundreds of metastables and polyatomic radicals and many paramagnetic ions remain to be discovered by l.m.r.; therefore, I predict that this highly sensitive tool will be used to measure dozens of new and exciting free radicals in the next few years.

#### FAR-INFRARED LASERS, FREQUENCY MEASUREMENT AND THE REDEFINITION OF THE METRE

The number of c.w. far-infrared lasing lines reported in Knight's recent tabulation<sup>62</sup> is 1350. Of these, about one-quarter oscillate in conventional l.m.r. spectrometers, and about one-half of these have been accurately (frequency) measured. In the operation of the spectrometer, the f.i.r. laser is tuned to the centre frequency of the lasing molecule by maximizing the laser power in single-mode operation. This adjustment is reproducible to *ca.*  $\pm 5 \times 10^{-7}$ , and does not drift outside this range during a spectral search.

The frequencies of these f.i.r. lasers are measured in separate experiments by synthesizing a frequency within a radiofrequency difference either from harmonics of microwave radiation or from difference frequencies between two CO<sub>2</sub> laser lines and possibly an additional X-band oscillator. It is this latter technique we have used<sup>63</sup> because it covers the entire far-infrared spectral region. A tungsten-nickel point-contact diode<sup>64</sup> is used as the non-linear element. The radiation from the f.i.r. laser, the two CO<sub>2</sub> lasers and the microwave oscillator (when needed) all radiate the tungsten antenna and electrons tunnel across the nickel oxide layer to the nickel base generating a radiofrequency difference. The far-infrared frequency difference,  $\nu_{f.i.r.}$ , is

$$\nu_{f.i.r.} = n(\nu_1 - \nu_2) \pm m\nu_\mu \pm \nu_b$$

where  $n$  is the harmonic of the CO<sub>2</sub> difference frequency,  $\nu_1$  is one CO<sub>2</sub> laser frequency,  $\nu_2$  is the other CO<sub>2</sub> laser frequency,  $m$  is the microwave harmonic,  $\nu_\mu$  is the microwave frequency and  $\nu_b$  is the r.f. difference frequency.

The uncertainty in this measurement is due to the uncertainty in finding the centre of the gain curve of the lasing medium  $\pm 5 \times 10^{-7}$ . Other uncertainties in determining  $\nu_{f.i.r.}$  are significantly less in most cases. To find the appropriate CO<sub>2</sub> lines, the frequency is first determined to an accuracy of <1 GHz by a wavelength measurement, made by measuring a number of half-wavelengths with the calibrated micrometer on the f.i.r. laser.

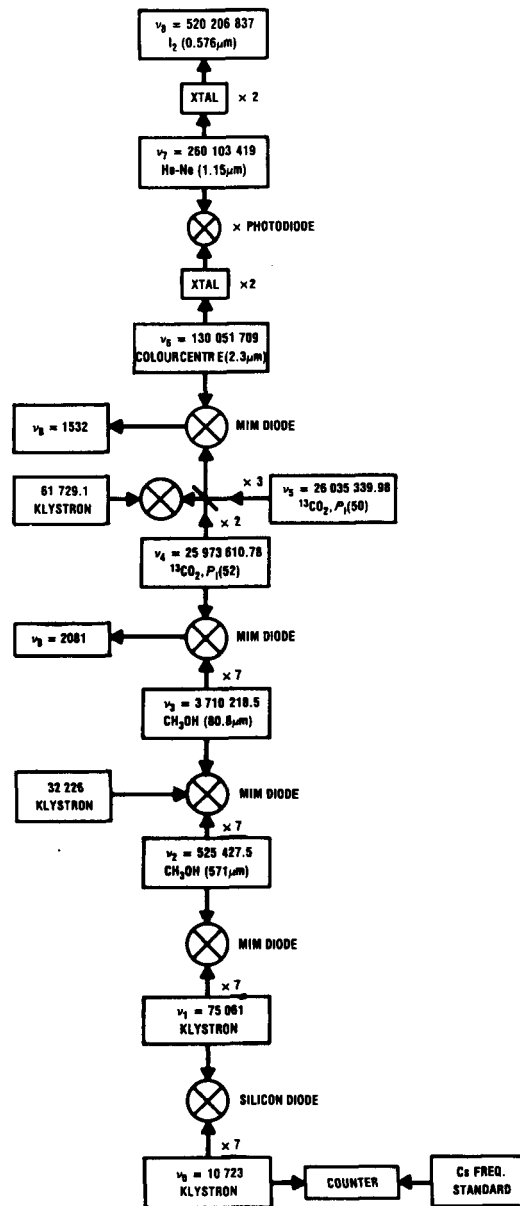


FIG. 2.—Laser frequency synthesis chain (to the visible). All frequencies in MHz.

The overall result is that the uncertainty in the f.i.r. laser frequency is *ca.*  $\pm 7 \times 10^{-7}$ . The uncertainty of  $5 \times 10^{-7}$  in setting the laser to the top of the gain curve is multiplied by  $2^4$  because the laser must be adjusted to the top of its gain curve two times: once when the frequency is measured, and once when the l.m.r. spectrometer is adjusted. We have not yet found it necessary to stabilize the f.i.r. cavity to the top of the gain curve.

While I am discussing laser frequency measurements, I would like to point out that

the frequency of visible light has recently been measured.<sup>65</sup> Frequencies can be measured orders of magnitude more accurately than wavelengths; therefore, the entire electromagnetic spectrum up to the visible is now accessible with ultra-high-resolution and extremely accurate frequency metrology. These events stimulated the Comité Consultatif Pour La Définition du Mètre in 1979 to propose a new definition of the metre: "The metre is the length equal to the distance travelled in a time interval of 1/299 792 458th of a second by plane electromagnetic waves in vacuum." This recommendation will be acted upon by the general conference of weights and measures in 1984.

The metre will be realized from this definition *via* a vacuum wavelength obtained from any stabilized laser whose frequency has been measured. The vacuum wavelength is, of course, the "fixed" value of  $c$  (299 792 458  $\text{ms}^{-1}$ ) divided by the measured frequency of that laser. It is therefore important that accurate frequencies of visible lasers be made. The first measurement of the frequency of visible light<sup>65</sup> was not of sufficient accuracy for realizing the "new" metre. Hence, more accurate measurements are now underway.

To extend frequency measurements to lasers, a series of steps are used in which harmonics of the radiation of one laser are heterodyned with the radiation from a higher-frequency laser to obtain a radiofrequency difference. The previously mentioned measurement of the frequency of visible light consisted of a "chain" of such harmonically related lasers connecting the caesium standard with the frequency of an iodine absorption in the visible. We are presently at work on a simpler and more accurate chain shown in fig. 2, connecting the caesium frequency with the same iodine frequency. The accuracy ultimately is limited by the accuracy of the caesium standard itself,  $\pm 1 \times 10^{-13}$ .

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