Prog. Quant. Electr. 1984, Vol. 8, pp. 143–151
Printed in Great Britain.

0079-6727/84 $0.00 + .50

OPTICAL FREQUENCY SYNTHESIS SPECTROSCOPY

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Abstract—In order to measure the super narrow spectral features of cooled atoms and ions, in the optical region, optical frequency synthesis (OFS) techniques rather than wavelength techniques must be used. It is anticipated that many of these resonances will be in the optical region of the spectrum, and this paper will address the state-of-the-art of the measurements of frequencies in that region. Two recent optical frequency measurements of iodine transitions in the visible will be described as well as recent improvements in fabricating the point-contact diode used in these measurements.

Key words—Optical spectroscopy, optical frequency synthesis (OFS), iodine.

1. INTRODUCTION

One of man's most accurate and precise endeavors is that of frequency measurement; therefore, it is not surprising that a significant part of his understanding of the physical world is through the application of these measurement techniques. Specifically, the extension of both frequency measurement and other radio frequency techniques to the optical region has made a significant impact on the fields of metrology and spectroscopy.

Optical frequency synthesis (OFS)[1] is an extension of radio and microwave frequency measurement techniques into the infrared and visible region of the electromagnetic spectrum. This advance has been made possible by the development of a source of radiation (the laser), sub-Doppler frequency stabilization techniques, and the broadband harmonic generating capability of metal–insulator–metal (MIM) diodes. OFS is a "bootstrap" method whereby harmonic combinations of spectrally pure and measurable lower frequency laser oscillators are used to generate higher laser frequencies. This technique has now been used to extend "direct" or "absolute" frequency measurements from the far infrared into the visible spectrum. Most importantly, direct frequency measurements are now being made in this visible region of the spectrum for the first time. It is in this region that the most accurate wavelength measurements traditionally have been made and the meter has been defined. Now we have two different methods for making excellent comparisons of radiations in the visible, one utilizing wavelength metrologic techniques and the other utilizing frequency metrology (OFS). At the current state of the art, wavelength comparisons are subject to inaccuracies of the order of a few parts in 10^{11} because of diffraction, imperfections in the optical components, etc. However, frequency comparisons can be made which are limited only by the quality of the oscillators and can be referred to a primary standard that is four orders of magnitude better than the primary length standard!

The metrologic significance of laser frequency measurement was first most clearly demonstrated in 1972 when both the frequency and wavelength of the methane stabilized He–Ne laser at 3.39 μm (88 THz) were accurately measured. The product of these is a value of the speed of light[2] 100 times more accurate than the value accepted at that time, a value limited only by the krypton primary length standard itself. The possibility of improving length metrology with the use of laser radiation, and also fixing the speed of light gave impetus to the Consultative Committee for the Definition of the Meter (CCDM) to propose a redefinition of the meter based on the second. In 1982 the CCDM proposed: "The meter is the length of the path travelled by light in vacuum during a time interval 1/299, 792, 458 of a second".[3]* With this definition, the meter could be realized using the wavelength of any laser which is stabilized

* On October 10, 1983, this new definition was formally adopted.

to a narrow atomic or molecular absorption feature for which the frequency is known. The wavelength, λ, would be determined from the relation $\lambda = c/\nu$, where c is the fixed value of the speed of light, and ν is the measured frequency of the stabilized laser. To realize this definition, it is necessary to accurately measure the frequency of certain absorption lines in the visible spectral region. The first such measurements were performed at NBS in the spring of 1982. Two iodine lines which are suitable for realizing the new meter were accurately measured with optical frequency synthesis techniques. The first of these lines,[4] a visible yellow iodine absorption line at 520 THz (576 nm), was measured using nonlinear crystals as frequency doublers above 130 THz (2.3 μm) and the MIM diode for harmonic generation at lower frequencies. This accomplishment was quickly followed by the measurement[5] of the red He–Ne iodine stabilized laser at 473 THz (633 nm), where the final frequency was synthesized by resonant enhanced four wave mixing of three known frequencies in a helium–neon plasma.

Additionally, because of the importance of the MIM diode to this technology, we shall describe some experiments which revealed improved coupling techniques and some surprising results concerning the sharpness of the diode tip which resulted in more stable diodes.

2. THE OFS MEASUREMENTS OF IODINE

We describe the measurement of the frequency of the *o* hyperfine component of the visible $^{127}I_2$ 17-1 P(62) transition at 520 THz (576 nm) and the *i* hyperfine component of the $^{127}I_2$ 11-5 R(127)-stabilized He–Ne laser[6] at 473 THz (633 nm) to 1.6 parts in 10^{10}. The frequencies were measured in three steps. First, a CO_2 laser line was compared with the CH_4-stabilized He–Ne laser at 88 THz (3.39 μm),[7] which presently is the most accurately known of all laser frequencies. Then, various CO_2 lasers referred to this CH_4 referenced laser were used in separate measurements of the 520 THz and 473 THz I_2 transitions. Since the 520 THz iodine line was used to measure the 473 THz frequency, the 520 THz frequency measurement will be discussed first.

The OFS technique here consists of a "chain" of lasers linking lower frequency lasers to higher ones with harmonic generation and heterodyning techniques as is shown in Fig. 1. In a MIM diode, three harmonics of one 26 THz CO_2 laser radiation plus two harmonics of another are heterodyned with the 130 THz color center laser radiation to produce a rf beat which is measured. Part of the color center laser radiation is subsequently frequency doubled and locked to the 260 THz He–Ne laser radiation. The He–Ne laser radiation is in turn frequency doubled and frequency locked to a 520 THz cw dye laser. The 520 THz cw dye ring laser at the top of the chain was servo-locked to the o hyperfine component of the $^{127}I_2$, 17-1 P(62) transition observed in saturated fluorescence. The line had a full width at half maximum of 1 MHz for an iodine pressure of 4 Pa. The center of the transition could be determined to within 40 kHz.

The He–Ne 260 THz laser employed an 8 m discharge tube and generated 100 mW of single mode output power. The He and Ne gas mixture was adjusted to optimize single mode output power. A resonant reflector with a thin lossy metallic film positioned 9 cm from the high reflectivity end mirror provided tuning and mode selection. Approximately 90 mW of the output power was focused into a temperature tuned lithium niobate frequency-doubling crystal ($T = 185°C$) to generate 50 μw of power at 520 THz. This visible radiation was collinearly mixed with a portion of the cw dye laser output on a Si photodiode to produce a rf beat used to lock the two lasers together.

The cw color center laser operating at 2.3 μm was used as a frequency transfer oscillator for connecting the He–Ne laser frequency to the accurately known CO_2 laser frequency. The color center laser used $(F_2^+)_A$ centers in lithium-doped KCl,[8] and provided broadly tunable laser output from 2 to 2.5 μm. When pumped with 4 W from a cw 1.33 μm Nd:YAG laser, the color center laser produced over 100 mW of output power at 2.3 μm. The laser was operated in a ring configuration to insure efficient single mode operation and was actively stabilized to a stable optical resonator with a resulting linewidth of less than 20 kHz.

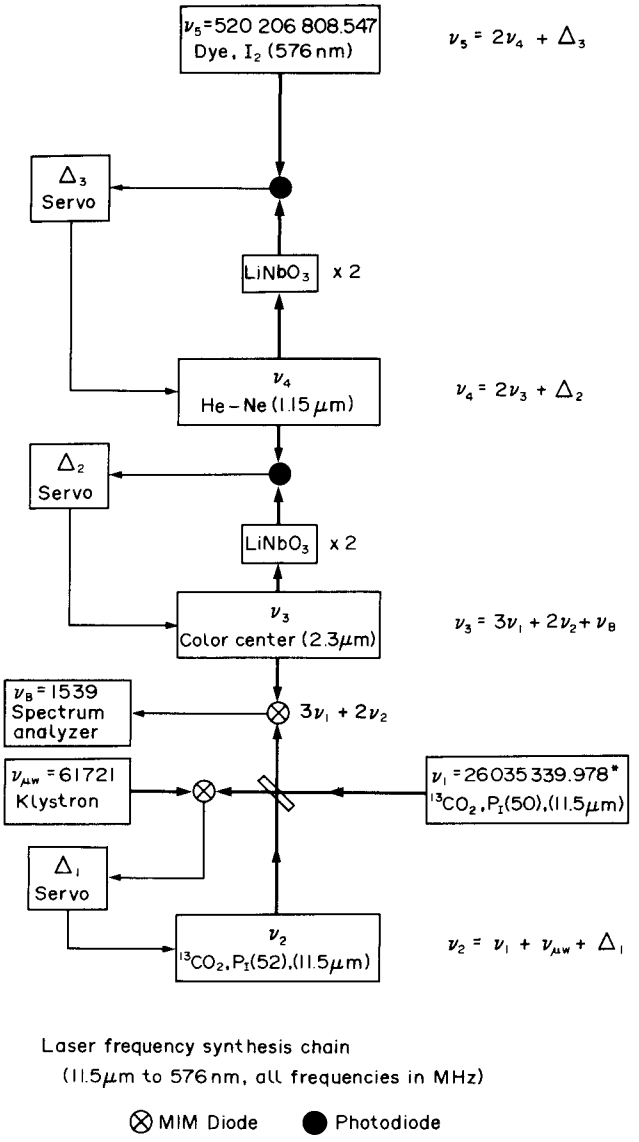

FIG. 1. The OFS chain for measuring 520 THz radiation.

The 2.3 μm radiation was focused into a temperature phase matched lithium niobate frequency-doubling crystal ($T = 530$°C) and generated approximately 10 μW of 1.15 μm radiation. This second harmonic output was combined collinearly on a beamsplitter with 10 mW from the He–Ne laser, and both beams were focused onto a high speed Ge photodiode. The resulting beat frequency was displayed on a rf spectrum analyzer and measured with an adjustable marker oscillator which was frequency counted.

The remainder of the non-doubled 2.3 μm radiation was focused onto a W-Ni point contact MIM diode. Coincident on the diode were the beams from two $^{13}C^{16}O_2$ lasers operating on the adjacent lines $P_I(50)$ and $P_I(52)$. The $P_I(50)$ laser was stabilized to the saturated fluorescence signal from an external 5.3 Pa $^{13}C^{16}O_2$ absorption cell. The $P_I(52)$ laser was phase locked to the $P_I(50)$ laser via a stabilized 62 GHz klystron. These two CO_2 lines were selected such that twice the frequency of one CO_2 laser plus three times the frequency of the other CO_2 laser nearly equalled the necessary color center laser frequency (130 THz). The free running CO_2 lasers each

had approximately a 3 kHz linewidth; however, the average frequency difference of the two lasers was held stable to within 1 Hz in a 1 s averaging period.

The frequency of the $P_T(50)$ laser was determined by comparing it with a CH_4-stabilized He–Ne laser operating at 88 THz. International intercomparisons have shown frequency reproducibility of this device to be about $\pm 3 \times 10^{-11}$, and a number of absolute measurements of its frequency have been reported.[3] We took the the average value of the four most recent measurements of this frequency as the basis for measurements described in this paper: the CH_4-stabilized He–Ne laser frequency was taken to be 88, 376, 181.609 MHz $\pm$ 0.009 MHz.

The result of the frequency chain measurement of the *o* hyperfine component of the $^{127}I_2$ 17-1 P(62) transition was

$$\nu_{I_2} = 520, 206, 808.547\ \text{MHz} \pm 0.081\ \text{MHz}.$$

This value is in agreement with previous, less accurate measurements.[9] The estimated frequency error represents a line center uncertainty of 1.6 parts in 10^{10}. Most of this uncertainty arises from the dispersion of the measured frequencies of the CH_4 standard, with the rest of the error appearing from effects such as reproducibility of the I_2 lock point, uncompensated pressure shifts, and counting and interpolation errors at each stage of the chain. Table 1 shows the error budget for this measurement.

The 633 nm He–Ne laser frequency was measured in a significantly different manner. Several years ago Klementyev *et al.* proposed a method of synthesizing 473 THz radiation using sum frequency mixing in Ne.[10] In this scheme, shown in Fig. 2, 473 THz radiation is generated by the nonlinear resonant mixing of radiation at the three measurable transition frequencies: 88 THz (3.39 μm), 125 THz (2.39 μm) and 260 THz (1.15 μm). The sum frequency at 473 THz is radiated by coherent polarization on the $3s_2$–$2p_4$ transition in Ne which results from the nonlinear interaction of the three fields resonant with three cascade transitions connecting the same two atomic levels. In our experiment, we used a separate laser for each of the frequencies and mixed them in a low pressure He–Ne discharge tube. The experimental arrangement is shown in Fig. 3. Summed in the tube were radiations at 88 THz from a CH_4-stabilized He–Ne laser (amplified to 8 mW), 125 THz from a 2.39 μm color center laser (50 mW) frequency-referenced to CO_2, and 260 THz from a 1.15 μm He–Ne laser (200 mW) referenced to I_2 at 520 THz. Approximately 5×10^{-8} W was generated at 473 THz. Mixing could be verified by blocking any one of the three input beams, which immediately caused the generated 473 THz red light to disappear or by frequency shifting any of the three source lasers which caused a corresponding shift in the synthesized frequency.

The 473 THz radiation from the summing tube was combined on a beamsplitter with 40 μW of radiation from a ^3He–^{20}Ne 473 THz laser stabilized on either the *g* or *i* hyperfine component

TABLE 1. Error budget for the 520 THz visible frequency measurement

Component	Error
1. CO_2 laser uncertainty (3.4 kHz times effectively 20 harmonics)[a]	68 kHz
2. Electronic resettability of entire I_2 servo system	40 kHz
3. Uncertainty in first derivative offsets and pressure shifts	15 kHz
4. Statistical fluctuation in data	14 kHz
Total Uncertainty (summed Quadratically)	81 kHz

[a]This 3.4 kHz is due to an estimated 1×10^{-10} uncertainty in the CH_4-stabilized He–Ne frequency added in quadrature to the measurement uncertainties in the determination of the $P_1(50)$ frequency (Ref. 7).

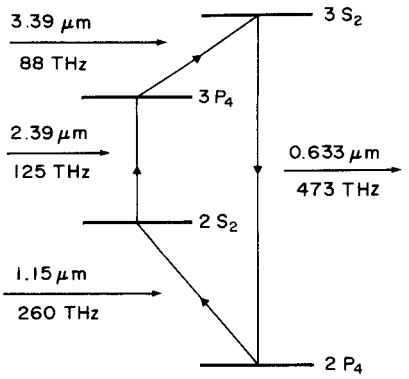

FIG. 2. Energy level diagram of Ne showing the pertinent cascade transitions used to synthesize 473 THz radiation.

of the $^{127}I_2$, 11-5, R(127) transition. From this beat and knowledge of the three infrared laser frequencies, the frequency of the *i*-component adjusted to the operating conditions recommended by the CCDM was determined to be

$$\nu_{I_2} = 473,\ 612,\ 214.830\,\text{MHz} \pm 0.070\,\text{MHz}$$

The estimated frequency error represents a line center uncertainty of 1.6 parts in 10^{10}. Again, most of this uncertainty arises from lack of knowledge of the CH_4 standard frequency, with the remainder due to uncertainty in the reproducibility of the lock points of both the I_2-stabilized He–Ne laser (1×10^{-10}), and of the I_2-stabilized second harmonic of the 1.15 μm laser. The error budget for the measurement is shown in Table 2.

Both visible frequency measurements described above represent an improvement in accuracy by almost 3 orders of magnitude over previous frequency measurements to the visible.[9]

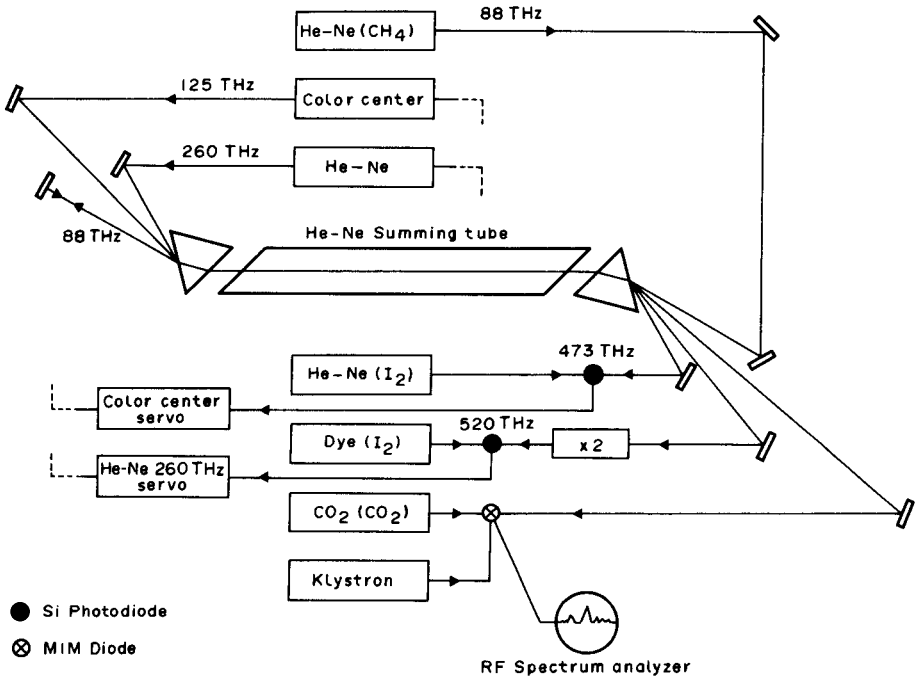

FIG. 3. Experimental apparatus for measuring the 473 THz laser frequency.

TABLE 2. Error budget for the 473 THz visible frequency measurement

Laser	Frequency in MHz	Measurement Uncertainty in kHz (independent of CH_4 uncertainty)	Correlated Uncertainty (due to CH_4 in kHz)
CH_4 88 THz	88, 376, 181.609	—	9
Color Center			
125 THz	125, 132, 754.610	11	12
I_2/2 260 THz	260, 103, 404.273	25	30
		27.4	51
$^{127}I_2$ 11-5 R(127)*g*	473 612 340.492	47	
$^{127}I_2$ 11-5 R(127)*i*	473 612 214.789[a]	47	
Total Uncertainty $[(27.4)^2 + (51)^2 + (47)^2]^{1/2} = 74$ kHz			

[a]The Comité Consultatif pour la Définition du Mètre[3] has recommended that the following conditions be realized when the $^{127}I_2$ molecule, transition 11-5, R(127), component *i* is used for intracavity stabilization of the 473-THz He–Ne laser: (1) I_2 cold-finger temperature of 15°C, (2) cavity standing-wave power of 40 mW, and (3) modulation peak-to-peak amplitude of 6 MHz. Therefore, the $^{127}I_2$ 11-5 R(127)*i* frequency adjusted for the recommended operating conditions is 473, 612, 214.830 ± 0.074 MHz.[5]

However, the uncertainty reported here does not yet approach the limits of this measurement technique, but is rather limited by the quality of the laser sources.[11] Our measurements were limited mainly by the frequency reproducibility of the lasers. Using the currently proposed redefinition of the meter, either of these lines could serve as a length standard with an improvement of about a factor of 10 compared to the present official length standard based on the ^{86}Kr discharge lamp. However, we have the techniques at this time to improve these or similar measurements by several orders of magnitude.

3. THE SPEED OF VISIBLE LIGHT

In order to check the accuracy of the value of the speed of light used in the new definition of the meter, a value of c using visible radiation is obtained by multiplying the value of the frequency of the red iodine absorption by the most accurately available wavelength value. The wavelength for this transition is obtained from four published values which are 632, 991, 399.0 ± 0.8 fm,[12] 632, 991, 399.8 ± 0.9 fm,[13] 632, 991, 400.0 ± 12. fm,[14] and 632, 993, 398.0 ± 3 fm.[15] The weighted average of these measurements is 632, 991, 399.4 ± 0.6 fm. The value for the speed of light is, of course, the product of the frequency and wavelength and is c = 299, 792, 458.6 ± 0.3 m/s, with a one sigma uncertainty.

This value of c, the most accurate ever measured for visible light, is in good agreement with the defined value of c proposed by the CCDM[14] and will, thus, maintain "continuity" in the meter with the new definition.

4. THE MIM DIODE

Metal–Insulator–Metal diodes in a point contact configuration, used at room temperature, are the most successful and versatile devices for absolute measurements of laser frequencies from the far infrared to the visible.[16] Field induced electron tunneling is the most widely accepted explanation for their extremely broadband response.[17–19] However, there is also some evidence for more than one phenomenon occurring in the diodes which contribute to the video detection at visible wavelegths.[20] Most experiments and theories have indicated that the contact area should be as small as possible in order to decrease the capacitance and hence minimize the time of response. Consequently, tip radii in the 40–90 nm range have been generally used. This feature seriously affects the mechanical stability of the diodes, sometimes preventing their use as routine laboratory devices. Also, delicate and short lived contacts can

make quantitative and systematic investigation of the physical mechanisms involved in detection and harmonic generation difficult.

Encouraged by a chance measurement at infrared frequencies in which video signals were almost unaffected with the use of a dull point, we performed more quantitative tests on the diode. Most of the interest in point contact MIM diodes lies in their high speed of response used in generating laser harmonics. In this experiment, that property was tested by the generation of third harmonic signals. Radiations from a 3.39 μm He–Ne laser at 88 THz and from a $R_I(30)$ CO_2 laser emission at 29 THz were focused on the diode with conical antenna coupling. Microwave power at 48 GHz from a phase-locked klystron also radiated the diode to produce a beat signal of a few tens of megahertz. After amplification in a broadband amplifier, the beat note with a singal-to-noise (S/N) ratio up to 25–30 dB in a 30 kHz bandwidth could be observed on a spectrum analyzer. The power focused on the diode was 30 mW from each of the lasers. The microwave power was in general adjusted to be close to the saturation power for the diode. The S/N ratio of the heterodyne signal was measured as a function of the resistance (adjusted mechanically) for each diode. The video sensitivity at 10 μm, 3.39 μm and 48 GHz was also recorded. Typically, the rectified signals increased almost linearly with the resistance up to about 1 kΩ and then showed some saturation (the signal at 2 kΩ was about 50% higher than the one at 1 kΩ). The shape of the video response vs the impedance was the same at 3.39 μm and 10 μm, but with a decrease of about two orders of magnitude in the detected signal strength at the shorter wavelength. With a resistance of 500 Ω, typical dc signals were 20 mV at 10 μm and 200 μV at 3.39 μm. The parabolic mirror used for focusing was machined for operation at wavelengths greater than 10 μm; therefore, a good share of the decrease was probably due to the optics. The measured dc signals were almost the same for all the tip radii between 50 and 760 nm with resistances below 1 kΩ. A small decrease (about 10%) in the sensitivity at higher resistance could be observed for the less sharp diodes. The beat S/N ratio was optimum for resistance values between 300 and 500 Ω with a gradual decrease of the signal at increasing resistance and a rapid decrease at lower values. Typical results are shown in Fig. 4. Diodes with four significantly different tip radii were used. No significant decreases in the S/N were observed from "sharp" to "dull" points. This is very surprising for the capacitance should be determined by the area of the

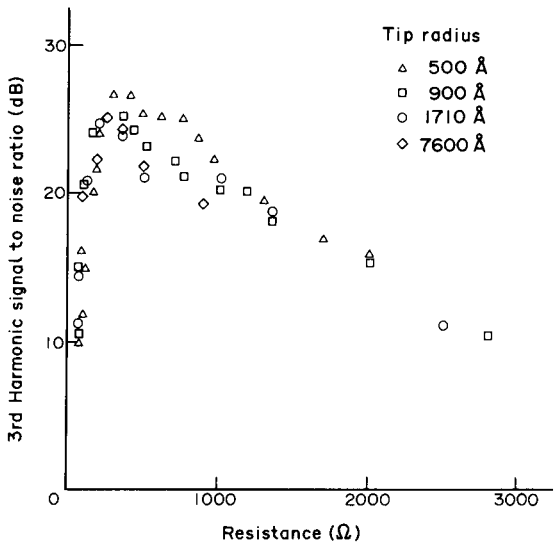

FIG. 4. Signal-to-noise ratios in a 30 kHz bandwidth for the observed beat signals in the third harmonic experiment as a function of the diode resistance. The beat was generated by the synthesis scheme $\nu_B = \nu_{3\cdot 39\,\mu m} - 3\nu_{R_I(30)} - 48.7$ GHz. Results for diodes with different tip radii of curvature are reported.

contact, i.e. the square of the tip radius. For a radius of some tens of nanometers, a frequency cut-off can be calculated of the order of 100 THz, and a radius of a few hundred nanometers should lead to a frequency cut-off two orders of magnitude lower. This is in complete disagreement with our experimental results. The "spreading resistance" in the base, proportional to the inverse of the contact radius, increases the RC time of response proportional to the radius,[21] but it, by itself, does not explain the high speed operation of these blunter diodes. Our measurements were performed to help understand the operation of the diode; however, they seem to have had the opposite effect. For instance, the "effective contact area" may not simply be determined by the square of the radius of the tip. It is, moreover, not clear how the dielectric constant of the oxide in the contact changes and affects the capacitance under the high mechanical and thermal stresses present when the contact is made.

These results, besides stimulting questions about the theory of operation of the diode, have pointed out a practical design improvement. With the use of less sharp tip radii, the stability of the diode has been dramatically increased without a significant decrease in the sensitivity or speed of response. The same contact can be stable for hours to days in normal laboratory environmental conditions without readjustment. Also, the diode resistance can be more precisely adjusted and reset with a resolution of a few tens of ohms. This is particularly important for the maximization of the beat S/N ratio in harmonic generation and mixing experiments. This experimental result opens a new theoretical puzzle and new possibilities for practical applications of the point contact MIM diodes. For instance, in the far infrared, the sensitivity is comparable to that of a Golay cell, but the speed of response is twelve orders of magnitude faster!

5. CONCLUSION

The application of OFS techniques to the measurement of the super narrow resonances from cooled atoms and ions will introduce a new era in spectroscopy. Optical frequency synthesis spectroscopy has already improved the accuracy of the spectral measurements of conventional spectra by two orders of magnitude compared with the use of wavelength techniques and promises further increases in accuracy. One possible application of the OFS technique could be the measurement of the Rydberg, which should be the first in a series of measurements promising unprecedented accuracy in our measurements of the fundamental constants. In this new era, measurements will be limited by ones ability to characterize the spectral features rather than the measurement techniques!

REFERENCES

1. A frequency synthesizer in the radio or microwave region of the spectrum has phase coherence between the synthesized frequency and a reference or standard. Optical frequency synthesis implies phase coherence in a given mixing step but not necessarily between steps, i.e. there is not necessarily phase coherence between the optical frequency and the reference frequency.
2. K. M. EVENSON, J. S. WELLS, F. R. PETERSEN, B. L. DANIELSON, G. W. DAY, R. L. BARGER and J. L. HALL, *Phys. Rev. Lett.* **29,** 1346 (1972).
3. Comité Consultatif pour la Définition du Metre, 7th Session, June 2–5, 1982 (Paris).
4. C. R. POLLOCK, D. A. JENNINGS, F. R. PETERSEN, J. S. WELLS, R. E. DRULLINGER, E. C. BEATY and K. M. EVENSON, *Opt. Lett.* **8,** 133 (1983).
5. D. A. JENNINGS, C. R. POLLOCK, F. R. PETERSEN, R. E. DRULLINGER, K. M. EVENSON, J. S. WELLS, J. L. HALL and H. P. LAYER, *Opt. Lett.* **8,** 136 (1983).
6. H. P. LAYER, *IEEE Trans. on Inst. and Meas.*, **IM-29,** No. 4 (1980).
7. F. R. PETERSEN, (private communication)
8. I. SCHNEIDER and C. L. MARQUARDT, *Opt. Lett.* **5,** pp. 214–15 (1980).
9. K. M. BAIRD, K. M. EVENSON, G. R. HANES, D. A. JENNINGS and F. R. PETERSEN, *Opt. Lett.* **4,** 263 (1979).
10. V. M. KLEMENTYEV, YU. A. MATYUGIN and V. P. CHEBOTAYEV, *ZhETF Pisma* **24,** 8 (1976).
11. See Ref. (7), and H. P. LAYER, W. R. C. ROWLEY and B. R. MARX, *Opt. Lett.* **6,** 188 (1981).
12. W. R. C. ROWLEY and A. J. WALLARD, *J. Phys.* **E6,** 647 (1973).
13. W. G. SCHWEITZER, JR., E. G. KESSLER, R. D. DESLATTES, H. P. LAYER and J. R. WHETSTONE, *Appl. Opt.* **12,** 2829 (1973).

14. Rapport: Comité Consultatif pour la Définition du Mètre, 5th Session, page M54 (1973) Bureau International des Poids et Measures, Sèvres, France.
15. G. R. HANES, K. M. BAIRD and J. DEREMIGIS, *Appl. Opt.* **12,** 1600 (1973).
16. K. M. EVENSON, D. A. JENNINGS and F. R. PETERSEN, *J. Phys. (Paris)* **42,** C8-473 (1981).
17. S. M. FARIS, T. K. GUSTAFSON and J. C. WIESNER, *IEEE J. Quant. Electr.* **QE-9** 737 (1973).
18. G. M. ELCHINGER, A. SANCHEZ, C. F. DAVIS, JR and A. JAVAN, *J. Appl. Phys.* **47,** 591 (1976).
19. A. SANCHEZ, C. F. DAVIS, K. C. LIU and A. JAVAN, *J. Appl. Phys.* **49,** 5270 (1978).
20. H. U. DANIEL, M. STEINER and H. WALTHER, *Appl. Phys.* **25,** 7 (1981).
21. D. J. E. KNIGHT and P. T. WOODS, *J. Phys. E. Scient. Instr.* **9,** 898 (1976).