

Ultrastable Optical Frequency Reference at 1.064 μm Using a C_2HD Molecular Overtone Transition

Jun Ye, Long-Sheng Ma, and John L. Hall

Abstract—Saturated molecular overtone transitions in the visible and near infrared can be detected with record-high sensitivities using our cavity-enhanced frequency modulation technique. We have stabilized a Nd:YAG laser onto the P(5) line in ($v_2 + 3v_3$) overtone band of C_2HD at 1.064 μm and established its absolute frequency. Excellent signal-to-noise ratio produced an Allan variance of 3.4×10^{-13} at 1 s averaging, improving to 1×10^{-14} after 800 s. Selection of slow molecules with low power and gas pressure gave a linewidth 13 times below the room temperature transit time limit.

I. INTRODUCTION

RECENTLY we have developed a new frequency modulation technique for detection of weak molecular absorptions located inside a high finesse cavity [1]–[3]. For standards work, the molecular transitions of principal interest are those vibrational-overtone lines covering the visible and near infrared regions because of their \sim ms-lifetimes. The potential of using saturated absorption techniques on these overtone lines to establish precise frequency references was only recently realized [4], [3]. Owing to the characteristic weak absorption by overtone transitions, the low-pressure sample gas is usually placed inside a high-finesse cavity. The cavity extends the effective cell length by the factor ($\text{Finesse} \cdot 2/\pi$), meanwhile it builds up sufficient internal power to have a discernible level of nonlinear interactions between light and molecules to yield narrow saturated absorption resonances. When the cavity is tuned onto a molecular line, a sizable part of the molecular signal will leak out of the cavity to reach a detector, while a similar portion of the input power will be transmitted by the cavity and reach the same detector to set the shot noise limit. The large intracavity buildup power, however, will remain trapped inside, after having phase-coherently prepared the molecular dipole moment. In order to suppress the large conversion of laser frequency noise to amplitude noise by the cavity discrimination, we use FM heterodyne spectroscopy of cavity-transmitted light. For this, we frequency modulate the input laser beam at exactly the

splitting frequency of the cavity free spectral range (FSR). The transmitted light through the empty cavity retains its pure FM characteristic and its heterodyne detection is insensitive to any (small) laser frequency noise. A useful signal will be produced only when one of the FM components is phase shifted or attenuated by the intra-cavity molecular dispersion/absorption.

The attractive property of laser frequency noise suppression of our method has led to the name of noise-immune cavity-enhanced optical heterodyne molecular spectroscopy (“NICE OHMS”). With this technique we are now detecting saturated molecular overtone transitions with ultrahigh sensitivities (2×10^{-12} integrated absorption, or $4.2 \times 10^{-14}/\text{cm}$ at 1 s averaging [5]. Recently improved to 6.7×10^{-13}). The resulting excellent signal-to-noise ratio (S/N) for these weak but narrow overtone lines has opened the door for realizing many high quality frequency references in the visible and near infrared. In this paper we demonstrate its potential by presenting our recent frequency stabilization result of locking a diode-pumped Nd:YAG laser (NPRO) to the P(5) line of the $^{12}\text{C}_2\text{HD}$ ($v_2 + 3v_3$) overtone band at 1064 nm. The Nd:YAG laser has been chosen as the leading candidate in many high precision scientific experiments: a few examples among many are coherent free-space optical communication, ground-based or space-borne gravitational wave detection, and measurement of the magnetically-induced birefringence of the QED vacuum. Consequently, the NPRO frequency stability has been driven to an ever higher level. Some pioneering work on Nd:YAG laser stabilization was done with cesium molecules [6]. A frequency-doubled Nd:YAG laser has been well-stabilized to hyperfine transitions in I_2 near 532 nm [7], [8]. With the narrower linewidth—but lower S/N—of the HCCD transition, we have currently achieved a level of stability similar to that of the I_2 system. However, owing to the long lifetime associated with overtone transitions, at low gas pressure and light power only slow molecules experience appreciable saturation. Therefore molecules can be optically selected for a long interaction time, leading to a much narrower linewidth than the room temperature transit time limit. The narrower line will eventually help to improve the long term stability and reproducibility.

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II. EXPERIMENTAL CONFIGURATIONS

Fig. 1 shows our experimental setup for high sensitivity spectroscopy of the P(5) line in the ($v_2 + 3v_3$) overtone band of $^{12}\text{C}_2\text{HD}$. Synthesized HCCD gas (81%/19% HCCD/HCCH

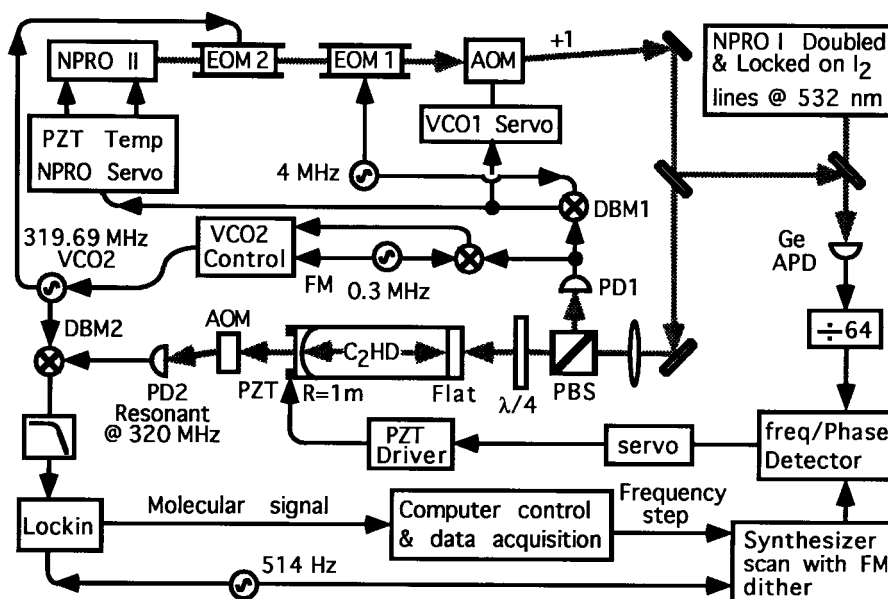


Fig. 1. Spectrometer setup for precision scanning of C_2HD overtone resonance at $1.06 \mu m$. Our sensitive detection concept is shown by EOM1 phase-modulating the laser beam at the cavity FSR frequency, providing noise-immune heterodyne detection of the transmitted light. DBM: double-balanced mixer; APD: avalanche photodiode.

by integration of the 1H NMR spectrum, $\sim 55\%$ chemical purity by a residual gas analyzer) is placed inside a cavity with a FSR of 319.695 MHz. One mirror was flat, the other had a 1 m radius of curvature. The intracavity beam waist was ~ 0.410 mm, dictating the room temperature transit time limit of 270 kHz full width at half maximum (FWHM) [9]. An empty cavity finesse of 31 900 was measured by a cavity-field ring-down method. By locking with a rf sideband technique based on detection of reflected light, the laser's full energy spectrum was narrowed and efficiently coupled into the cavity. The electrooptical modulator 1 (EOM1) produced the locking FM sidebands at 4 MHz. An acoustooptic modulator (AOM) and the NPRO's internal piezoelectric transducer (PZT) served as the frequency servo transducers. The servo gain was sufficient to provide a low frequency-noise-density of $0.15 \text{ Hz}/\sqrt{\text{Hz}}$, corresponding to a 0.07 Hz laser linewidth relative to the cavity. Phase modulation of the laser beam at the FSR frequency was generated by the resonantly-coupled EOM1 and detected in cavity transmission by an InGaAs p-i-n diode in a resonant RF tank circuit. The modulation signal was provided by a low phase noise crystal voltage-controlled-oscillator (VCO). Its frequency was locked onto the cavity FSR by the 300 kHz FM dither also detected in cavity reflection. This loop ensured the noise immune property during the cavity scan by tracking the VCO frequency to match the changing cavity FSR [10]. Modulation index of ~ 0.5 was chosen so that the central carrier still effectively saturated the molecular absorption while the sidebands were large enough to give a strong heterodyne cross term. An isolation AOM directly after the cavity prevented optical feedback from the detector. Subsequent phase sensitive demodulation yielded the molecular dispersion signal.

To establish an absolute frequency mark and reference for scanning, another NPRO was frequency doubled and locked onto an I_2 reference at 532 nm [8]. The heterodyne beat

signal between the two NPRO's (after digital phase division by 64) was phase locked to a synthesizer. To improve S/N and baseline stability, we modulated the cavity frequency around the molecular resonance by an FM dither on the synthesizer and used an audio lock-in for signal recovery. Although the 150 kHz NPRO/cavity servo bandwidth already leads to a gain of ~ 70 dB at our 514 Hz cavity dither frequency, for the best results we also used feed-forward of the dither signal directly onto the NPRO PZT. The same synthesizer was then frequency stepped by a computer to force the cavity/NPRO system to scan out the molecular resonance. Signal averaging over many scans (~ 1 min each) was available with the long-term stability of the NPRO/ I_2 system in the sub-100 Hz domain. This is essential in our current stage of slow molecules detection due to a limited S/N, resulting from the low input power of 1 mW and < 2 mtorr gas pressure we typically used (1 torr = 133 Pa).

For testing the quality of this C_2HD overtone resonance as an optical frequency standard at $1.064 \mu m$, we locked the NPRO/cavity system onto the line and measured the heterodyne beat against the known NPRO/ I_2 reference system [8]. An analog sine-wave dither signal (typically equivalent to 800 kHz peak-to-peak) at 1 kHz was directly applied onto the PZT of the C_2HD cavity. The rf-detected dispersion signal in transmission was used with 2nd harmonic detection on the lock-in to obtain a "third-derivative" discrimination signal which was integrated and then fed onto the cavity PZT. A 75 mW optical power was used for input to the cavity and 3.5 mW was received by the detector after the cavity. (A post-cavity optical attenuator was needed to reduce the cavity output to this safe level for our detector.) We found 10 mtorr was the optimum gas pressure for a maximum slope of the molecular locking error signal, by taking into account the combined parameters of linear absorption, saturated absorption hole depth and the pressure broadened linewidth.

III. EXPERIMENTAL RESULTS

For our 10 mtorr sample gas, we measured its linear absorption through our 46.9-cm long cavity (single pass) to be 1.6×10^{-7} , leading to an absorption coefficient of $6.2 \times 10^{-7}/\text{torr} \cdot \text{cm}$ for pure HCCD, in good agreement with the available band strength data [11]. The present cavity has a resonant transmission efficiency of 41% which decreases by 1.3×10^{-3} near the Doppler profile peak (a contrast of 0.32%). Tuning onto the saturation resonance increases the maximum transmission by 138×10^{-6} , corresponding to a saturation depth of 10.6%. From a 75 mW input light, the high finesse cavity had a power buildup to 300 W, giving a saturation parameter of ~ 0.46 at 10 mtorr.

For a molecular frequency reference operating at a certain pressure, it is important to study the pressure dependent linewidth broadening and line center shift. At each fixed gas pressure that we chose to measure the linewidth, we varied the input light power to measure the power broadening. By knowing the saturation at each pressure, we were then able to find the power broadening contribution to the linewidth and make corresponding corrections by extrapolating to zero power. With this method we have found a pressure broadening (FWHM) coefficient of 34.7 ± 0.8 MHz/torr. We note that earlier results of pressure broadening on other C-H bond molecules such as CH_4 [12] and C_2H_2 [2] yielded 32.6 ± 1.2 and 29.8 ± 0.1 MHz/torr respectively. These large broadening coefficients may be due in part to the sensitivity of saturated absorption to velocity-changing collisions. The zero-pressure, zero-intensity extrapolated linewidth was 290 ± 7 kHz, very near the value of 270 kHz set by the transit time. We can summarize these results by an expression for the saturation intensity: $I_{\text{sat}} = 6103 (\Gamma_T + 34.7 P)^2 \text{ W/mm}^2$, where Γ_T is the FWHM (in MHz) associated with transit-time [9], and P is the pressure in torr. The equivalent saturation power in the free-flight regime is 117 W inside, reduced to 29.3 mW input by the cavity enhancement of 4000. We have also measured a pressure shift of the line center $\sim +250$ ($\pm 20\%$) Hz/mTorr with our current sample gas. A more thorough investigation of the line center shift versus pressure with various gas chemical compositions is underway.

Fig. 2 shows the molecular discrimination signal obtained by the 2nd harmonic detection on the lockin with 10 mtorr gas. The linewidth (FWHM) of 920 kHz included contributions from transit-time, pressure and power broadenings. The line shape accurately follows Wahlquist's modulation-broadening formalism for a dispersion signal [13]. With the saturated absorption in the 1.7×10^{-8} domain, we obtained a S/N of 8700 at 1 s averaging, ~ 1.6 times above the calculated shot noise limit. This level of S/N set the frequency standard deviation when the NPRO laser was locked on the molecular line.

It is interesting to compare this C_2HD -stabilized laser with another NPRO stabilized on I_2 resonances. In Fig. 3 the counted beat frequency vs time shows a drift ~ 20 Hz/h. The slowly-increasing noise in the beat was due to the less-than-perfect cavity vacuum system which gradually changed the intracavity gas composition. NPRO I (after frequency

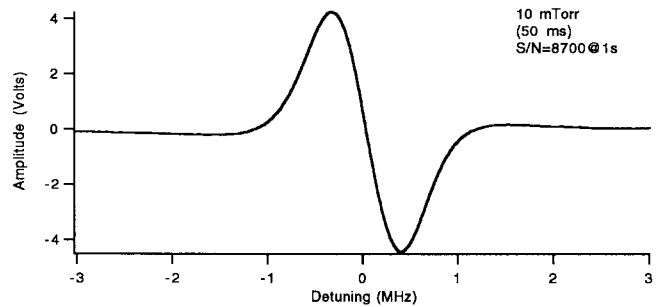


Fig. 2. Molecular discrimination signal used for stabilizing NPRO, obtained by the 2nd harmonic detection of the molecule dispersion.

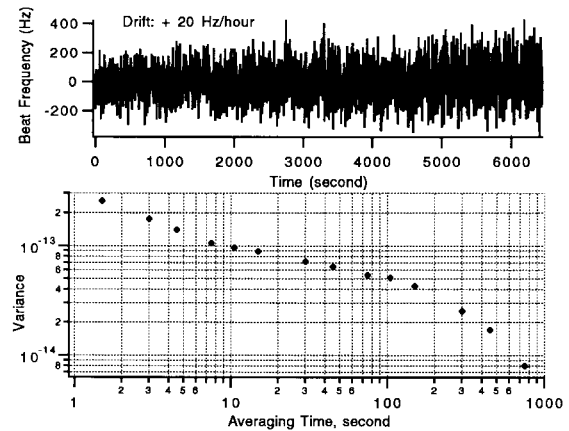


Fig. 3. Time record of the beat frequency between the two NPRO's, one locked on the C_2HD overtone transition, the other was frequency doubled and locked on an I_2 reference at 532 nm, which is 5252.2261 ± 0.0026 MHz lower. Allan variance is calculated from this data.

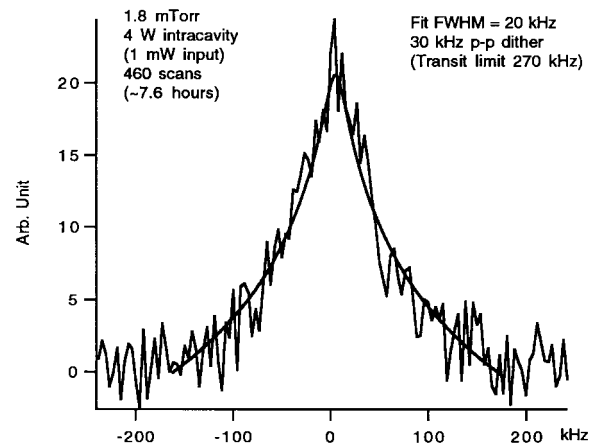


Fig. 4. With low power and gas pressure, slow molecules give a linewidth 13 times below the transit limit.

doubling) was locked on I_2 : R(56) 32-0, component a_{10} [8], [2]. With the mean value of the beat frequency between the two lasers at 5252.2261 ± 0.0026 MHz, we determined the absolute frequency of the P(5) line in the $(v_2 + 3v_3)$ band of $^{12}\text{C}_2\text{HD}$ to be $281\,635\,363.962 \text{ MHz} \pm 20.2 \text{ kHz}$. The 20 kHz uncertainty is mainly due to the limited knowledge of the absolute frequency of the NPRO/ I_2 , a secondary standard. At 1 s averaging we obtained a frequency noise of ± 100 Hz, in direct agreement with the S/N available at $1.064 \mu\text{m}$. (The

NPRO/ I_2 reference system had a 20 Hz rms, 4×10^{-14} frequency noise at 1 s as tested with a second I_2 spectrometer.) The corresponding Allan variance of $\sigma_Y = 3.4 \times 10^{-13}/\sqrt{\tau}$ improves to 1×10^{-14} at a longer integration time (>800 s), a promising indicator for an ultrastable frequency reference. The visible noise bump around ~ 200 s on the Allan variance diagram was associated with the lab room temperature cycling period.

Linewidth narrowing is offered by slow molecules since the natural lifetime of the overtone transition is about 300 times longer than our current transit time [14]. The cavity input power was reduced 75 times from our maximum available power to 1 mW. A low power is necessary so that the low Rabi frequency leads to appreciable saturation only for the slowest molecules. In our <2 mtorr sample gas, the mean-free-path of molecules is ~ 30 times longer than the transverse field dimension, thereby creating the so-called transit-time regime. The saturation now becomes inhomogeneous, with molecules from different transverse velocity groups contributing different intensities and widths. Slow molecules which spend their whole lifetime inside the field will have a constant and velocity-independent saturation parameter, controlled primarily by the collisional broadening. Considering their shorter interaction times, faster moving molecules will see a reduced saturation and will mostly contribute to the wings of the resonance. Fig. 4 shows a resonance with a linewidth of ~ 20 kHz, without correction for the modulation broadening by a 30 kHz peak-to-peak dither of the cavity. This is 13 times narrower than that set by the room temperature transit-time-limit, and is mainly limited by the relatively high pressure (1.8 mtorr). With out computer-based scan system, we are ready to explore the limit of our detection sensitivity with a much lower pressure. At present the limited S/N associated with the low power has prevented us from taking full advantage of this narrow linewidth. With an improved system this approach will enable us to access the information of free molecules with minimized second order Doppler shift, thereby creating an optical frequency standard of potentially high accuracy.

IV. CONCLUSION AND FUTURE OUTLOOK

With a molecular C_2HD overtone transition, we have demonstrated a valuable optical frequency reference at $1.064 \mu\text{m}$ using out sensitive detection method of NICE OHMS. After 800 s integration, an Allan variance of 1×10^{-14} was recorded. Slow molecules have been optically selected and a thirteen-fold linewidth reduction was observed. We have started building another NPRO/ C_2HD system, with a cavity finesse exceeding 100 000. The intracavity mode size will be increased three-fold by a 52 m radius of curvature mirror, reducing the transit time limit to ~ 90 kHz. With the increased detection sensitivity, we should be able to improve our short term frequency noise to ~ 30 Hz (1×10^{-13}) at 1 s averaging. A linewidth of a few tens of kHz with an improved S/N offered by slow molecules will help to maintain a high level of long term stability and reproducibility. Meanwhile ultrahigh resolution spectroscopy of these and

other molecular overtone transitions will also be conducted with the aim to resolve hyperfine structures and recoil splittings, a qualitatively new regime of molecule overtone transition research.

Considering the weak absorbing nature of this particular overtone line, we are exploring the possibility of using stronger overtone transitions to further improve the S/N and consequently the frequency stability. These lines do exist, even in the visible, lying within the tuning ranges of diode or Ti:Sapphire lasers (see [1] for example). It is certainly ambitious but not far-fetched to expect a 1×10^{-14} short term stability at 1 s averaging, with a line ten times stronger than ours. Work along this direction is already in progress.

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REFERENCES

- [1] L-S. Ma, J. Ye, P. Dubé, and J. L. Hall, "A new modulation method for sensitive nonlinear spectroscopy—application to molecular overtones as visible frequency references," *Laser Spectroscopy XII*, M. Inguscio, M. Allegrini, and A. Sasso, Eds. Singapore: World Scientific, 1996, p. 199.
- [2] J. L. Hall, J. Ye, L-S. Ma, S. Swartz, P. Jungner, and S. Waltman, "Optical frequency standards—some improvements, some measurements, and some dreams," in *5th Symp. Freq. Standards Metrology*, J. C. Bergquist, Ed. Singapore: World Scientific, 1996, p. 267.
- [3] J. Ye, L-S. Ma, and J. L. Hall, "Sub-Doppler optical frequency reference at $1.064 \mu\text{m}$ by means of ultrasensitive cavity-enhanced frequency modulation spectroscopy of a C_2HD overtone transition," *Opt. Lett.*, vol. 21, p. 1000, 1996.
- [4] M. de Labacherie, K. Nakagawa, and M. Ohtsu, "Ultrathin $^{13}C_2H_2$ saturated-absorption lines at $1.5 \mu\text{m}$," *Opt. Lett.*, vol. 19, p. 840, 1994.
- [5] L-S. Ma, J. Ye, P. Dubé, and J. L. Hall, "Ultrasensitive cavity-enhanced FM spectroscopy of C_2H_2 and C_2HD molecular overtone transitions," unpublished.
- [6] A. A. Mak, S. G. Muravitsky, O. A. Orlov, and V. I. Ustyugov, "New laser for interferometry with long-term frequency stabilization at $1.06 \mu\text{m}$ onto molecular cesium standard," in *Proc. SPIE*, vol. 1121, p. 478, 1989.
- [7] A. Arie and R. L. Byer, "Laser heterodyne spectroscopy of $^{127}I_2$ hyperfine structure near 532 nm," *J. Opt. Soc. Amer. B*, vol. 10, p. 1990, 1993.
- [8] P. Jungner, M. Eickhoff, S. Swartz, J. Ye, J. L. Hall, and S. Waltman, "Absolute frequency of the molecular iodine transition R(56) 32-0 near 532 nm," *IEEE Trans. Instrum. Meas.*, vol. 44, p. 151, 1995; M. L. Eickhoff, Ph.D. dissertation, Univ. Colorado, Boulder, 1994.
- [9] C. J. Bordé, J. L. Hall, C. V. Kunasz, and D. G. Hummer, "Saturated absorption line shape—calculation of the transit-time broadening by a perturbation approach," *Phys. Rev. A*, vol. 14, p. 236, 1976.
- [10] A related concept was explored by A. Morinaga, private communication to J. L. Hall, Aug. 1995.
- [11] M. Tamsamani, J. Vander Auwera, and M. Herman, "The absorption spectrum of C_2HD between 9000 and 13000 cm^{-1} ," *Mol. Phys.*, vol. 79, p. 359, 1993.
- [12] R. L. Barger and J. L. Hall, "Pressure shift and broadening of methane line at 3.39 microns studied by laser-saturated molecular absorption," *Phys. Rev. Lett.*, vol. 22, p. 4, 1969.
- [13] R. L. Smith, "Practical solutions of the lock-in detection problem for Lorentz and dispersion resonance signals," *J. Opt. Soc. Amer.*, vol. 61, p. 1015, 1971.
- [14] S. N. Bagayev, V. P. Chebotayev, A. K. Dmitriyev, A. E. Om, Y. V. Nekrasov, and B. N. Skvortsov, "Second-order Doppler-free spectroscopy," *Appl. Phys.*, vol. B 52, p. 63, 1991; and C. Chardonnet, F. Guernet, G. Charton, and C. J. Bordé, "Ultrahigh-resolution saturation spectroscopy using slow molecules in an external cell," *Appl. Phys.*, vol. B59, p. 333, 1994.



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