Absolute Frequency Atlas of Molecular I_2 Lines at 532 nm

Jun Ye, Lennart Robertsson, Susanne Picard, Long-Sheng Ma, and John L. Hall

***Abstract*—With the aid of two iodine spectrometers, we report for the first time the measurement of the hyperfine splittings of the P(54) 32-0 and R(57) 32-0 transitions near 532 nm. Within the tuning range of the frequency-doubled Nd : YAG laser, modulation transfer spectroscopy recovers nine relatively strong ro-vibrational transitions of $^{127}I_2$ molecules with excellent SNR. These transitions are now linked together with their absolute frequencies determined by measuring directly the frequency gaps between each line and the R(56) 32-0 : a_{10} component. This provides an attractive frequency reference network in this wavelength region.**

***Index Terms*—Frequency control, frequency measurement, frequency modulation, laser spectroscopy, laser stability, measurement standards, YAG lasers.**

I. Introduction

THERE has been increasingly strong support in the optical frequency/wavelength metrology community to adopt the molecular iodine transitions near 532 nm [1] as one of the next generation visible standards. The initial demonstration of the system performance proves to be highly successful in terms of the practicability, reliability, and the high-frequency stability the system offers [2]. Absolute frequency measurement has been carried out on a well-isolated hyperfine component of one of the transitions [3], namely R(56) 32-0 : a_{10}, using secondary standards such as the iodine-stabilized 633 nm HeNe laser and the rubidium D_2 and two-photon lines [4]. A new measurement is reported in these proceedings [5]. In this paper, we report two new iodine lines [6] lying about 50 GHz red of the R(56) 32-0 : a_{10} resonance. These lines are interesting since they are both strong and are actually closer to the gain center of the latest commercially-available models of the diode-pumped all solid-state Nd : YAG lasers [7]. With two iodine spectrometers available for heterodyne experiment, the hyperfine splittings of the two new lines have been measured and then fitted to a four-term hyperfine Hamiltonian. Cross-beating between the two spectrometers shows an improved frequency stability of the iodine-stabilized lasers. An Allan standard deviation of 5×10^{-14} at 1-s averaging time has been obtained. Altogether, we have nine different I_2 ro-vibrational transitions with reasonable strengths in the 532 nm region. Their transition frequencies are also given in the paper, relative to the R(56) 32-0 : a_{10}, with uncertainties mainly due to the presently-limited accuracy of R(56) 32-0 : a_{10}.

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II. I_2 Transistions Near 532 nm

The sub-Doppler modulation-transfer I_2 spectrometers are constructed similarly to the ones reported earlier, along with the setup of the Nd : YAG laser frequency-doubling [2]. However, in both spectrometers we have lowered the normal operating temperature of the I_2 cells cold-fingers to (-15 to -20) °C, corresponding to a range of I_2 vapor pressure of (0.787 to 0.436) Pa. For frequency metrology work, the use of low sample pressure is important in terms of both minimizing the collision-induced pressure shift and reducing the influence on the baseline by the linear Doppler background. The signal size will of course decrease as the pressure goes down; however, the light path length inside the cell can be extended using a multipass strategy or even cavity enhancement. In our current work, the 1.2-m cell length is already long enough to give adequate SNR ($\sim$120 in a 10 kHz bandwidth). Another important aspect of using lower pressure is that a smaller optical power is needed to saturate the transition, yielding a smaller power-related center frequency shift. For the work of laser frequency stabilization, the overall reduction of the operational resonance linewidth can to a certain degree compensate for the loss of the signal size since it is the ratio of the linewidth versus the signal size which determines the residual rms frequency noise of the stabilized laser.

Following the notations in [2], we label our two spectrometers as East (E) and West (W). The FM modulation frequency on the pump beam in the E(W) spectrometer is 350 (317) kHz, with a modulation index of $\sim$0.9 (provided by electrooptic modulators). The lower modulation frequencies (compared with previous choices) reflect the fact of narrower linewidth that we are now dealing with. In the West spectrometer, we typically use a pump (probe) power of 1.0 (0.26) mW. The collimated beam diameters are $\sim$1.9 mm, with the probe beam cross section slightly smaller than the pump beam.

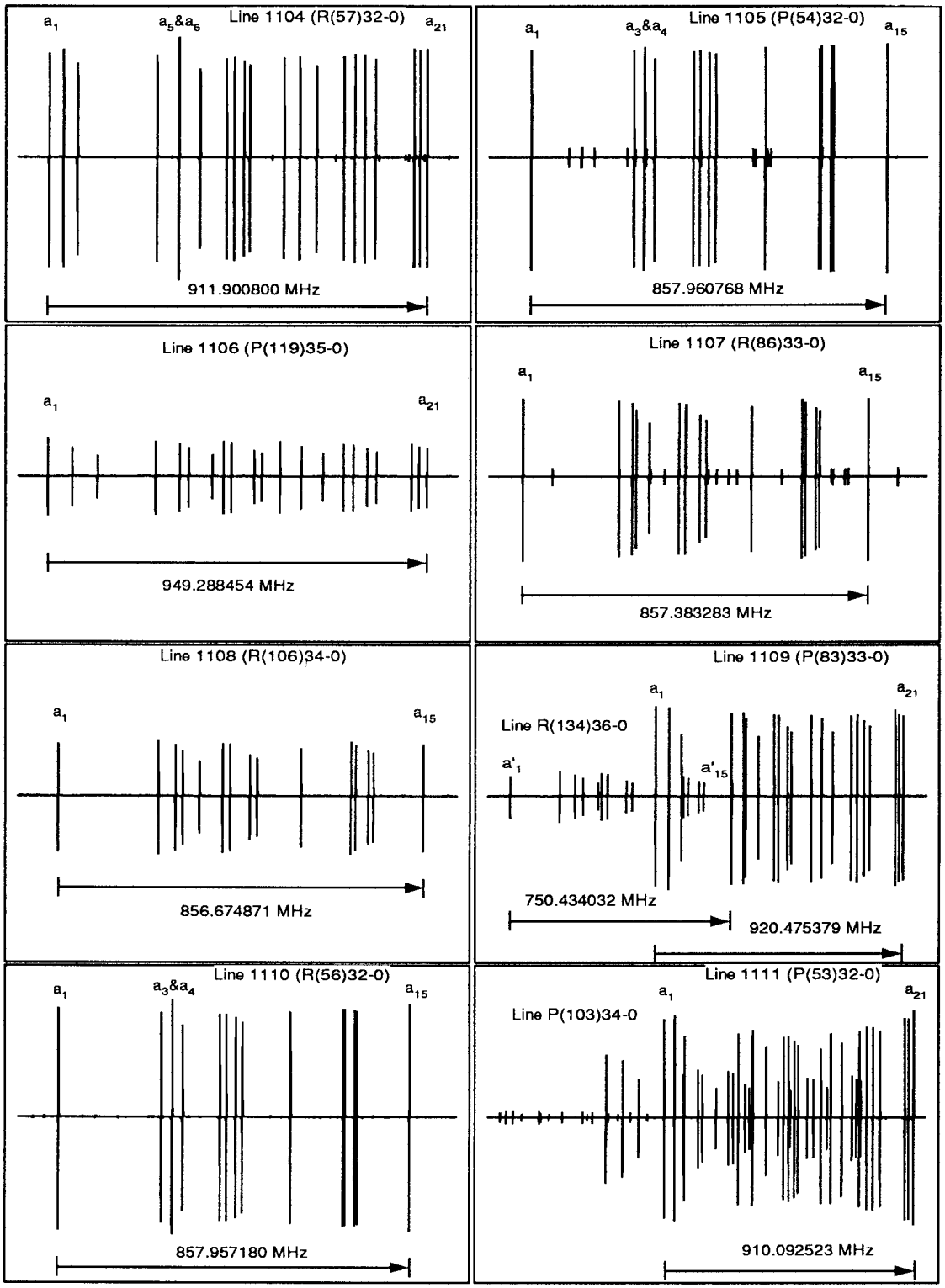

Fig. 1. I_2 hyperfine transitions at 532 nm, within the tuning range of the frequency-doubled Nd:YAG laser. The I_2 cell cold finger temperature is -15 °C (258K).

The counter-propagating pump and probe beams are cross-polarized with normal incidence to the cell windows. In the East spectrometer, we have added a pair of beam expanders for additional control of the beam profiles, which are usually twice as large as the West beams. The East cell windows are Brewster cut and two 45° Faraday rotators are used to produce parallel linear polarization for both beams. The pump (probe) power is ~2.2 (0.5) mW, which gives about half of the saturation compared to that in the West.

Fig. 1 shows the hyperfine structure of the ten different ro-vibrational lines of the $^{127}I_2$ molecule near 532 nm. The notation for the line designation is borrowed from [8]. The

frequency scale is calibrated by counting the heterodyne beat signal between the two YAG lasers, one being locked on a certain I_2 transition while the other one is scanning through the interested spectral feature. The resonance signal is low-pass filtered with a time constant of 5 ms and recorded by a computer data acquisition board. The general pattern of the $^{127}I_2$ (nuclear spin 5/2) hyperfine structure follows the symmetry considerations. For even (odd) J numbers of the ground rotational states, the total spin of the two nuclei is odd (even), resulting in 21 (15) hyperfine sublevels. The sub-Doppler structure of lines 1104 (R(57)32-0) and 1105 (P(54)32-0) is being reported here for the first time. Crossover transitions are clearly visible in the scans of R(56) 32-0 and R(57) 32-0. However, some other resonances of intermediate strengths such as those in the scan of line 1105 are due to transitions from excited vibrational ground states.

III. Beat Frequency Measurement and Uncertainties

Heterodyne experiments between the two I_2-stabilized lasers offer the most direct check of the system performance, such as the frequency stability and the long-term reproducibility. We detect the beat signal both at the fundamental wavelength (1.064 mm) and at the frequency-doubled green output. The advantage of using the modulation transfer technique on the external cell is again evident in the form of the clean and unmodulated cw output from the laser.

The modulation transfer signal of the molecular resonance is properly filtered and demodulated before being sent to the servo amplifier and then to the laser's internal piezoelectric transducer (PZT) for frequency error correction. Care is taken to generate a reasonably large signal size directly after demodulation while avoiding any spurious RF pickup. Optical isolation and reduction of scattering light are also critical for the frequency stability. For example, there should be absolutely no scattered pump light (which carries the modulation information) entering the probe photo detector.

Control of the I_2 pressure is maintained by the temperature stabilization of the cell's cold finger. We note, however, that it is still important to have a relatively good temperature uniformity around the entire I_2 cell, especially if we are ambitious to demand the best performance from the system. In one of our heterodyne tests, we recorded the beat frequency between the two lasers when a sudden temperature step was applied to one of the I_2 cell cold fingers. It took about 5 min for the laser frequency to attain 80% of its total frequency shift, but it took almost 30 min to reach the equilibrium. We believe that this double-exponential time evolution is associated with rapid pumping of the gas-phase molecules, followed by slower desorption and reabsorption of the I_2 molecules from the cell walls by the finite pumping ratio of the cold finger. Another significant temperature effect is due to the normal-incidence cell windows, which give rise to the unwanted etalon modulation on the FM components of the incident pump beam. We have to actively control the temperature of the window substrate when the fluctuation of the laboratory room temperature is noticeably large.

Fig. 2 shows the time record of the beat frequency when both lasers are locked on the same transition of R(56) 32-0 : a_{10}. The beat is measured in the infrared with the counter gate time of 1 s. The standard deviation of the beat frequency noise is ~20 Hz, corresponding to ~14 Hz rms noise per IR laser at 1-s averaging time. This result directly translates into an Allan standard deviation of 5×10^{-14} at 1 s. With longer times up to ~100 s, the Allan deviation decreases, basically following the slope of $1/\sqrt{\tau}$, with τ being the averaging time. After 100 s, the variance reaches the flicker floor at $\sim 6.5 \times 10^{-15}$. What is remarkable for a visible optical frequency standard is to reach the frequency (in)stability of 1×10^{-14} under just 1 min. And we stress that no additional optical cavities are used for prestabilizing the laser frequency.

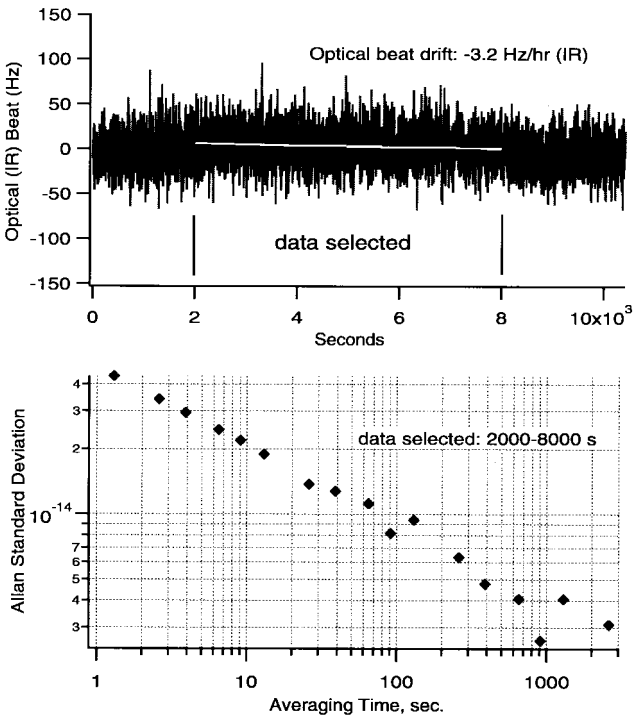

Fig. 2. Time record of the beat frequency between the two iodine-stabilized Nd:YAG lasers, with a 1-s gate time. The Allan standard deviation is calculated from this data.

With the knowledge of the absolute frequency of R(56) 32-0 : a_{10}, it is certainly attractive to link the frequencies of other neighboring transitions (see Fig. 1) directly to this component. Hyperfine splittings within a given ro-vibrational line can be measured with relative ease since the involved frequency gaps are within a 1 GHz range. Therefore, we have chosen to measure the distances from the a_1 components of each ro-vibrational transition to the frequency mark, line R(56) 32-0 : a_{10}. [Except for line 1109 (P(83)33-0) where the component a_{21} is used instead, owing to the contamination of a_1 by another nearby resonance.] Fig. 3 summarizes the measurement result. Large frequency gaps are bridged by using a low noise local oscillator to feed into a harmonic mixer to down-convert the beat note from the 60 GHz fast photodiode [9]. The data presented here are the average of the measurements taken in both spectrometers, with different iodine cells, FM modulation frequencies, beam sizes and intensities, as well as different beam polarization arrangement.

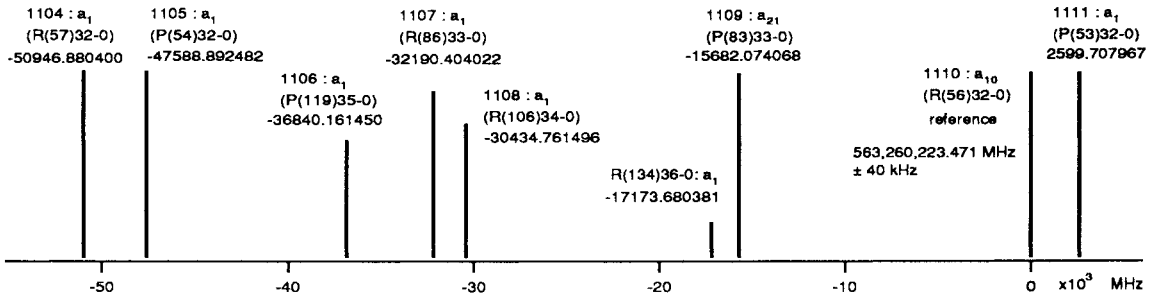

Fig. 3. Frequency atlas of the I_2 transitions at 532 nm, measured relative to the R(56) 32-0 component a_{10}, whose absolute frequency is known to within ± 40 kHz.

TABLE I

HYPERFINE INTERVALS OF R(57)32-0 AND P(54)32-0, COMPARISON BETWEEN MEASUREMENTS AND FIT. EQUAL WEIGHTS ARE USED FOR THE FITTING. NO CALCULATION IS PERFORMED FOR THE a_5 AND a_6 COMPONENTS OF R(57)32-0 SINCE THEY ARE NOT RESOLVED IN OUR SPECTROMETERS. ALSO, THE a_3 AND a_4 COMPONENTS OF P(54)32-0 ARE SPACED CLOSELY TOGETHER AND WERE NOT USED. HYPERFINE CONSTANTS OF THE GROUND STATES FROM YOKOZEKI AND MUENTER [11] (ONLY AVAILABLE FOR $v'' = 0$, $J'' = 13$)

EQ"q -2452.583 700(1600); C" 0.003 162(8); d" 0.001 580(50); δ" 0.003 660(30)							
Hyperfine constants of the excited states derived from the fit here. (All units in MHz)							
P(54) 32 - 0 (line 1105): Fit RMS: 0.000 384 standard deviation: 0.000 448							
eQ'q -544.151 568(879); C' 0.089 268(1); d' -0.042 530(52); δ' -0.007 064(57)							
comp	F'	I	J	observed	calculated	obs-calc	weight
a_1	53	2	53	0.000 000	0.000 000	0.000 000	1.0000
a_2	49	4	53	260.992 396	260.991 843	0.000 553	1.0000
a_3	54	2	53	285.007 708	285.008 489	-0.000 781	1.0000
a_4	52	2	53	286.726 354	286.726 083	0.000 271	1.0000
a_5	57	4	53	310.066 414	310.066 398	0.000 016	1.0000
a_6	50	4	53	402.249 461	402.250 176	-0.000 715	1.0000
a_7	51	4	53	417.667 671	417.667 983	-0.000 312	1.0000
a_8	55	4	53	438.918 557	438.918 347	0.000 210	1.0000
a_9	56	4	53	454.563 403	454.563 512	-0.000 109	1.0000
a_{10}	53	4	53	571.536 448	571.535 775	0.000 673	1.0000
a_{11}	51	2	53	698.613 569	698.613 719	-0.000 150	1.0000
a_{12}	52	4	53	702.934 816	702.934 717	0.000 099	1.0000
a_{13}	54	4	53	725.833 932	725.833 701	0.000 231	1.0000
a_{14}	55	2	53	731.687 908	731.687 957	-0.000 049	1.0000
a_{15}	53	0	53	857.960 804	857.960 933	-0.000 129	1.0000
R(57) 32 - 0 (line 1104): Fit RMS: 0.000 614 standard deviation: 0.000 691							
eQ'q -544.203 186(1120); C' 0.089 577(1); d' -0.042 694(80); δ' -0.006 755(65)							
comp	F'	I	J	observed	calculated	obs-calc	weight
a_1	53	5	58	0.000 000	0.000 000	0.000 000	1.0000
a_2	58	1	58	39.371 794	39.371 314	0.000 480	1.0000
a_3	63	5	58	76.827 726	76.828 393	-0.000 667	1.0000
a_4	54	5	58	273.041 640	273.042 421	-0.000 781	1.0000
a_7	59	3	58	375.283 770	375.283 555	0.000 215	1.0000
a_8	57	3	58	438.242 910	438.243 816	-0.000 906	1.0000
a_9	62	5	58	456.183 368	456.184 289	-0.000 921	1.0000
a_{10}	55	5	58	479.200 670	479.201 481	-0.000 811	1.0000
a_{11}	56	3	58	492.915 106	492.915 600	-0.000 494	1.0000
a_{12}	60	3	58	573.916 618	573.916 717	-0.000 099	1.0000
a_{13}	61	3	58	610.925 138	610.924 768	0.000 370	1.0000
a_{14}	55	3	58	650.805 214	650.804 643	0.000 571	1.0000
a_{15}	58	3	58	715.549 514	715.550 230	-0.000 716	1.0000
a_{16}	61	5	58	741.175 334	741.174 663	0.000 671	1.0000
a_{17}	56	5	58	764.715 986	764.715 134	0.000 852	1.0000
a_{18}	57	5	58	789.776 692	789.775 829	0.000 863	1.0000
a_{19}	59	5	58	881.115 742	881.116 220	-0.000 478	1.0000
a_{20}	60	5	58	895.015 562	895.015 699	-0.000 137	1.0000
a_{21}	57	1	58	911.901 232	911.900 902	0.000 330	1.0000

However, the disagreement between the two JILA setups is typically within ± 300 Hz.

We note that there is a frequency difference existing between the two spectrometers, which manifests itself as a nonvanishing offset in the beat frequency when both lasers are locked on the same transition. The offset is about 1.4 kHz (in green), after taking the power shifts into account. This could be partly due to the difference of the long term drifts of the I_2 cells. Our present setups do not give us an easy access to the interchange of the two cells between the spectrometers. Over a short time scale (1 month), this offset is almost constant, as each system can reproduce itself quite well in the daily operations.

IV. Hyperfine Splittings of R(57) 32-0 and P(54) 32-0

Hyperfine splitting measurement is also carried out via the heterodyne technique, under relatively small optical powers so that the crossover resonances are at least 100 times smaller than the main peaks. Frequency pulling effects due to these small but potentially dangerous resonances are then minimized. However, we still find that hyperfine interval values determined from the East spectrometer, where the beam intensity is about half of that in the West, produce a slightly better fitting to the theoretical calculations. Consequently, we report only the results from the East spectrometer in Table I.

The Hamiltonian of hyperfine interaction, expressed in Table I, includes four contributing terms, namely the electric quadrupole, spin-rotation, tensorial spin-spin, and scalar spin-spin interactions [10]. From the experimental data of the main hyperfine transitions ($\Delta F = \Delta J$), we are able to extract the information only about the difference of the hyperfine constants between the ground and excited state. Hence, for the ground state hyperfine constants we simply use the values from [11] (corresponding to the same vibrational ground state but a different rotational state, $J'' = 13$), which represent the closest approximation available. The hyperfine constants of the excited states for both P(54)32-0 and R(57)32-0 transitions are then given in Table I, along with their respective uncertainties. The standard deviation of the fit is on the order of 500 Hz.

It would be very useful to excite the so called "crossover" transitions between the main $\Delta F = \Delta J$ lines and the much weaker $\Delta F = 0$ resonances. Although the crossover resonances are about $1/(2J)$ less intense than the main lines, they will however grow much faster in size than the main lines when the input optical power is increased in a saturation spectrometer. This is simply because the main lines have already been operated in the saturation regime while the crossovers can still grow linearly thanks to the unsaturated $\Delta F = 0$ transitions. Knowing the positions of these crossovers would help to determine the ground state hyperfine constants and so provide a full solution for the hyperfine structure. For the purpose of frequency metrology, it is also important to map out these crossovers since a chosen transition for the frequency mark should lie a safe distance away from any small and yet perturbing resonances. On the technical side, we certainly do not welcome crossover resonances to contaminate the otherwise clean spectral window in which we place our FM modulation frequency. Work along this line is already under progress in our laboratory [12].

V. Conclusions

The I_2-stabilized solid-state Nd : YAG laser system clearly shows a strong performance both in the realization of a simple optical frequency standard and in the high-precision tests of the molecular physics. These results come as no surprise since the I_2 transitions at 532 nm are strong and narrow (100 kHz to 200 kHz). The high SNR and the flat baseline associated with the modulation-transfer signal-recovery strategy help to bolster the frequency stability. We may be able to recover even narrower resonances, albeit of weaker transition strengths, with similar or even higher SNR's using high-sensitivity approaches such as the cavity-enhanced frequency modulation technique [12].

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Jun Ye, for photograph and biography, see this issue, p. 536.

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Long-Sheng Ma, for a photograph and biography, see this issue, p. 536.

John L. Hall, for a photograph and biography, see this issue, p. 536.