Large optical depth frequency modulation spectroscopy

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Band-resolved frequency modulation spectroscopy is a common method to measure weak signals of radiative ensembles. When the optical depth of the medium is large, the sensitivity drops exponentially and the technique becomes ineffective. In this situation, we show that the sensitivity can be recovered when a larger modulation index is applied. Noticeably, the signal can be dominated by the natural linewidth of the resonance, regardless of the presence of inhomogeneous line broadening. We implement this technique on a cesium vapor, and explore its main spectroscopic features. In particular, we improve the precision of the atomic linewidth measurement as the optical depth increases.

Band-resolved frequency modulation spectroscopy was proposed in 1980 by G. Bjorklund, as a new method to measure weak absorption and dispersion signals [1]. Here, the carrier frequency of the laser is scanned across the resonance under investigation. In the weak modulation index limit, the amplitude and phase modifications of the carrier are encoded in the beat note with the first sidebands. Band-resolved FM-spectroscopy and its variant as Pound-Drever-Hall [2, 3], or modulation transfer spectroscopy [4–6] are key laser spectroscopic techniques which are used for laser frequency stabilization [7, 8], Doppler-free spectroscopy [9–11], detection of gases [12–16], and strain sensors [17, 18].

At large optical depth (OD), the carrier is strongly absorbed and the usual FM-spectroscopy method is ineffective. By increasing the modulation index, so that the spectrum is dominated by the weakly absorbed first and second sidebands, we will show that we recover a FM-spectroscopic signal with comparable sensitivity. In this setting, we probe the tails of the resonance coming from the slow algebraic decay of the homogeneous linewidth, rather than the faster exponential decay of some frequency broadening mechanisms, such as Doppler effect. Thus, the spectroscopic signal is dominated by the homogeneous linewidth of the transition, which can be measured more precisely as the OD becomes larger.

We consider an incident laser of intensity $I_0$ undergoing a frequency modulation. Using the Jacobi-Anger expansion, the incident electric field reads,

$$E_i(t) = E_0 \sum_{n=-\infty}^{+\infty} i^n J_n(\beta)e^{-i(\omega+n\Omega)t},$$  \hspace{1cm} (1)

where $E_0$ is the field amplitude, $J_n(x)$ is the $n$-th order Bessel function of the first kind, $\beta$ is the modulation index, $\omega$ is the optical frequency, and $\Omega$ is the modulation frequency.

As a first insightful approach, we consider the transmission of the laser through a two-level atomic vapor at $T = 0$, where $T$ is the vapor temperature. More general cases involving multi-line atomic transition and non-zero vapor temperature will be addressed later. The transmit-
The maximal slope magnitude $4J_0J_1e^{-1/\Gamma} \simeq 0.5/\Gamma$ is obtained for $b_0 = 2$, $\beta = 1$ [black dashed line in Fig. 1(a)], the product $J_0J_1$ being maximal at $\beta = 1$.

For large OD, the usual FM-spectroscopy becomes ineffective because of the large absorption of the carrier [see Eq. (7)]. Increasing $\beta$ to 2.4, we find an interesting configuration where the laser power is mainly distributed in the first and second sidebands. Considering only these sidebands, the magnitude and phase of the demodulated signal slope at $\Delta = 0$ is [19],

$$\frac{S_D}{I_0} = \frac{3}{2} J_1 J_2 b_1 \exp \left( -\frac{5}{8} b_1 \right) \Gamma^{-1}, \quad \Phi_D = \frac{\phi_1}{2}. \quad (8)$$

where $b_1 = b_0 \Gamma^2/(4\Omega^2)$ and $\phi_1 = b_0 \Gamma/(4\Omega)$ are the OD and phase shift respectively at $\Delta = \Omega$, i.e., at the detuning of the first sidebands when the carrier is on-resonance. The sideband components at the tails experience phase shifts that are sensitively dependent on the OD and the modulation frequency. Thus, the phase of the demodulated signal that results from the beat note between these sidebands is also parameter-dependent. The maximal slope amplitude of $12J_1J_2e^{-1}/(5\Gamma) \simeq 0.2/\Gamma$ is obtained for $b_1 = 8/5$, see Fig. 1(b). Importantly, we note that the maximal slope amplitude has a value comparable to the standard low modulation index FM-spectroscopy.

Consider now a two-level atomic vapor with non-zero temperature, the bulk susceptibility becomes

$$\chi_T = \frac{1}{\sqrt{2\pi} \nu} \int dv \exp \left( -\frac{v^2}{2\nu^2} \right) \chi(\Delta - kv). \quad (9)$$

where $\nu = \sqrt{k_BT/m}$, $k_B$ and $m$ are respectively the thermal velocity, the Boltzmann constant, and the atomic mass. For large $\Omega$ ($\Omega > 150\Gamma$ in the example depicted in Fig. 1(d)), one recovers the full sensitivity with a behavior matching the $T = 0$ case in Fig. 1(b). Indeed, we are probing the tails of the transmission spectrum, which are dominated by the homogeneous linewidth of the transition. More precisely, one gets a Doppler-free signal using a single frequency-modulated laser beam, whereas the $\beta = 1$ case shows poor sensitivity [see Fig. 1(c)]. For a fair comparison between the zero and the finite temperature cases in Fig. 1, we use $b_0$ which corresponds to the OD of the gas at $T = 0$. At a finite temperature, the measured OD is $b_T = b_0g(k_B \nu/\Gamma)$ where $g(x) = \sqrt{\pi/8} \exp (1/8x^2) \text{erfc}(1/\sqrt{8x})/x$ [20]. For large $x$, $g(x) \simeq \sqrt{\pi/8x}$.

The high-index FM-spectroscopy experiment is performed on a 7 cm cesium vapor cell as depicted in Fig. 2(a). The temperature of the cell is set in the range of 20-85 °C, corresponding to $b_T = 3-700$ (or $b_0 = 200-50000$). A 852 nm laser (Toptica DL pro) is scanned around the $F = 4 \rightarrow F' = 3, 4, 5$ transitions of the D2 line of cesium (natural linewidth: $\Gamma_0/2\pi = 5.2$ MHz). A local oscillator, at $\Omega = 706.8$ MHz, drives an EOM.
Figure 2. (a) The experimental setup and the cesium energy level diagram. (b)-(c) The magnitude and phase of the demodulated signals at $T = 53 \, ^\circ$C. The detuning $\Delta$ is referenced with respect to the $F = 4 \rightarrow F' = 5$ transition. The experimental results are plotted in blue, whereas the predictions of the model are plotted in red. In (b), the minimum of the demodulated signal, indicated by the black dashed line, is identified as the spectrum center $\Delta_c$. The spectrum center also corresponds to the point where the phase experiences rapid shift by $\pi$, as indicated by the black dashed line in (c). (d) Demodulated signal components, phase rotated to have the maximum slope. The different colors represent different vapor temperatures. (e) The magnitude (blue curve) and phase (red curve) of the theoretical demodulated signal of a two-level medium with the same $b_0$ and $T$ as that in (b) and (c).

to generate the phase modulation. The maximal modulation index is $\beta = 2.14(10)$, slightly lower than the optimum value of 2.4, which should lead to a moderate reduction of the sensitivity by 4%. Using a fast detector, a mixer, a delay line, and a low pass filter, the transmission signal through the cesium vapor is demodulated at $\Omega$. The DC transmission spectrum is also measured, see [19]. The laser frequency is calibrated on a standard saturated absorption spectroscopy setup.

Figs. 2 (b)-(c) show the magnitude and the phase of the demodulated signal taken at a temperature of 53 °C ($b_0 = 53000$). Other spectra at different temperatures are presented in [19]. The shape of the spectrum (blue curves) is non trivial, but well captured by Eq. (6) (red curves), taking into account the hyperfine structures of the excited state and Doppler broadening, while ignoring the Zeeman manifold. The sub-Doppler structure, observed at the spectrum center in Figs. 2 (b)-(c), narrows down as the temperature increases. This point is illustrated in Fig. 2(d), where we fully transfer by phase rotation, the linear slope at the spectrum center, $\Delta_c$, to the $I'_p$ component of the demodulated signal leaving the other component $I'_q$ to have a slope of zero at $\Delta_c$ [19].

Fig. 2(e) shows the predicted demodulated signal of a two-level medium, for the same $b_0$ and $T$ as that in Fig. 2(b) and (c). Most of the spectrum complexity is already present in the two-level case, suggesting that the oscillations in the signal comes from the rapid phase rotation of the transmitted field for a large OD medium, rather than from the hyperfine structure of the cesium D2 line. However, the two-level medium shows a zero amplitude signal at resonance, since the symmetry of the spectrum leads to the exact cancellation at resonance between the contributions of the negative and the positive sidebands. Because $I'_P$ and $I'_Q$ are odd functions, the phase gets an abrupt jump of $\pi$ at resonance. When several atomic transitions contribute to FM-spectroscopy, like for the cesium D2 line, the spectrum becomes asymmetric and the exact cancellation of the contribution of
Figure 4. (a) The RSS curves at $T = 83^\circ\text{C}$. (b) The curvature at the minima of the RSS curves. In both panels, the blue curves (triangles) result from the fit of the transmission spectra only, while the red curves (circles) include also the demodulated signals.

the negative and the positive sidebands does not occur. Nevertheless, the magnitude of the modulated signal still exhibit a minimum that we take as the spectrum center $\Delta_c$ [black dashed line in Fig. 2(b)]. In Fig. 3(a), the measured $\Delta_c$ at different temperature are shown as green open circles. They are compared to the model (blue curve). The values are plotted against $b_1$, defined here as the average value of the OD at the +1 and −1 sidebands. We find a good agreement between theory and experiment, but the spectrum center varies significantly for small ($b_1 < 0.04$) and large ($1 < b_1 < 10$) values of $b_1$. At large values of $b_1$, there are multiple minima in the modulated signals, which vary in their positions as $b_1$ changes. This leads to the abrupt jumps observed in this regime (see [19] for more details). The OD-dependence of the spectrum center can be a limitation for precise spectroscopic measurement and laser locking application. However, it turns out that at larger modulation frequency and larger $b_0$ [see the red curve curve in Fig. 3(a)] the variation of the spectrum center with $b_1$ can be strongly suppressed and the spectrum center coincides with the transitions geometrical center [black dashed line in Fig. 3(a)] defined as $\sum_i S_i \omega_i / \sum_i \omega_i$, where $S_i$ is the transition strength factor and $\omega_i$ its optical frequency.

We then compute the derivative of the demodulated signal at the spectrum center, to extract the frequency sensitivity of the signal. The experimentally measured slope values [see green open circles in Fig. 3(b)] are in good agreement with the model (blue curve). At larger OD and modulation frequency, the sensitivity is expected to reach the maximal value of $0.2/\Gamma$ as predicted by the Eq. (8).

Finally, we explore the possibility of using the demodulated signals to extract important parameters of the system. We illustrate this point on the determination of the homogeneous linewidth $\Gamma$ of the transitions. We first fit only the transmission spectra and calculate its residual sum of squares (RSS). The fitting procedure is performed for different fixed values of $\Gamma$ in the range $(0.1-10)\Gamma_0$. One example of the RSS dependence on $\Gamma/\Gamma_0$, at high temperature ($T = 83^\circ\text{C}$), is shown as the blue curve in Fig. 4(a). We then improve the sensitivity to $\Gamma$ by including the two components of the demodulated signals to the fit. The calculated RSS is divided by 3 for a fair comparison between the two cases [red curve in Fig. 4(a)]. To quantify the increase in the sensitivity, we calculate the curvature of each RSS curve at its minimum, see Fig. 4(b) [19]. Above $T = 70^\circ\text{C}$, the curvature for the fits involving the demodulated signals (red curve), increases clearly above the corresponding values for the fits of solely the transmission spectra (blue curve).

In conclusion, we presented a new sensitive FM-spectroscopic technique relevant at arbitrarily large OD. Using high modulation index, the sample is probed with the detuned sidebands. When the modulation frequency becomes much larger than the Doppler width, these sidebands probe the tails of the resonance, which are dominated by the homogeneous response of the vapor. Thus, this method becomes Doppler-free and further shows high sensitivity at large OD. We implement the large OD FM-spectroscopy on the D2 line of a cesium thermal vapor, and find a good agreement with our model. The complex shape of the demodulated signal leads to an accurate estimation of the transition linewidth. Applications might be found in precision measurement of pressure broadening in bulk atomic vapor where surface effect can be safely ignored [21–23]. Furthermore, large OD FM-spectroscopy could be an efficient tool to probe collective responses, including cooperative Lamb shift, Lorentz-Lorenz shift and dipole-dipole interaction in dense atomic medium [24].These studies are usually performed on thin vapor cells [25], small cold atomic clouds with low OD [26, 27], and thin penetration layers through selective reflection measurements [28], where finite size effects are important. Here again, this technique can be used on a medium of thickness much greater than one wavelength of the light, where the OD is large at high density. Then, the bulk response of the medium can give the dominant contribution. Finally, even though we explored this technique on an atomic vapor, it can be generalized to other types of media, such as dye or other molecular solutions, Mie scatterers ensemble, point-defects in diamond, and heavily doped glasses and crystals.

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Supplemental Material:
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I. EXPRESSION FOR THE DEMODULATED SIGNALS

We consider an incident field that is phase modulated,

$$E_i(t) = E_0 e^{-iωt+iβ\cos Ω}.$$  (S1)

Using the Jacobi-Anger expansion and the relation

$$J_{-n}(x) = (-1)^n J_n(x),$$

one gets

$$E_i(t) = E_0 \sum_{n=-∞}^{∞} i^n J_n(β) e^{-i(ω+nΩ)t},$$  (S2)

which is Eq. (1) of the paper.

The field transmitted through a dilute two-level medium is given by

$$E(t) = E_0 \sum_{n=-∞}^{∞} i^n J_n(β) e^{-i(ω+nΩ)t} B_n(Δ).$$  (S3)

The function $B_n(Δ)$ is the transmissivity of the $n$-th sideband, where $Δ$ is the detuning of the carrier frequency.

Since we focus on the linear regime, by neglecting the effect of saturation, $B_n(Δ)$ does not depend on the intensity of the light field. The transmitted intensity is then given by

$$I(Δ, t) = I_0 \sum_{n, m} i^n J_n(β) J_m(β) e^{-i(n-m)Ω} B_n(Δ) B_m^*(Δ),$$  (S4)

where $n$ and $m$ are summed over all integers. The transmission signal consists of a DC component (at $m = n$) and all harmonics of $Ω$. The DC component of the transmission is calculated to be

$$I_{DC}(Δ) = I_0 \sum_{n=-∞}^{∞} J_n^2(β) |B_n(Δ)|^2.$$  (S5)

The first harmonic of the transmitted intensity is given by

$$I_1(Δ, t) = I_0 \sum_{n=-∞}^{∞} \left[ J_n(β) J_{n-1}(β) B_n(Δ) B_{n-1}^*(Δ) e^{-iΩt} - J_n(β) J_{n+1}(β) B_n(Δ) B_{n+1}^*(Δ) e^{iΩt} \right]$$

$$= 2I_0 \sum_{n=-∞}^{∞} J_n(β) J_{n+1}(β) \left[ \text{Im} \left\{ B_n(Δ) B_{n+1}^*(Δ) \right\} \cos Ω t + \text{Re} \left\{ B_n(Δ) B_{n+1}^*(Δ) \right\} \sin Ω t \right].$$  (S6)

Using again the relation $J_{-n}(x) = (-1)^n J_n(x)$, we can rewrite the above summation with only positive values of $n$,

$$I_1(Δ, t) = 2I_0 \sum_{n=0}^{∞} J_n(β) J_{n+1}(β) \left[ \text{Im} \left\{ B_n(Δ) B_{n+1}^*(Δ) - B_{-n}(Δ) B_{-n-1}(Δ) \right\} \cos Ω t \right.$$  

$$+ \left. \text{Re} \left\{ B_n(Δ) B_{n+1}^*(Δ) - B_{-n}(Δ) B_{-n-1}(Δ) \right\} \sin Ω t \right].$$  (S7)

The in-phase and in-quadrature components of the demodulated signal is related to $I_1$ through

$$I_P(Δ) = I_0 \sum_{n=0}^{∞} J_n(β) J_{n+1}(β) \text{Im} \left\{ B_n(Δ) B_{n+1}^*(Δ) - B_{-n}(Δ) B_{-n-1}(Δ) \right\},$$

$$I_Q(Δ) = I_0 \sum_{n=0}^{∞} J_n(β) J_{n+1}(β) \text{Re} \left\{ B_n(Δ) B_{n+1}^*(Δ) - B_{-n}(Δ) B_{-n-1}(Δ) \right\}.$$  (S8)
In the complex notation, we have

\[ I_d(\Delta) \equiv I_P + iI_Q = iI_0 \sum_{n=0}^{+\infty} J_n(\beta)J_{n+1}(\beta) \left\{ B_n^*(\Delta)B_{n+1}(\Delta) - B_{-n}(\Delta)B_{-n-1}^*(\Delta) \right\}. \]  

(S9)

Under this complex notation, the first harmonic intensity is

\[ I_1 = 2\text{Re}\left\{I_d e^{-i\Omega t} \right\}. \]  

(S10)

We can rewrite

\[ I_1 = 2\text{Re}\left\{I_d e^{i\varphi} e^{-i(\Omega t + \varphi)} \right\}. \]  

(S11)

Thus, variation by \( \varphi \) of the phase of the local oscillator used to demodulate the signal, results in a complex demodulated signal that is rotated by \( \varphi \) in the complex plane, i.e.,

\[ I_d' = I_de^{i\varphi}. \]  

(S12)

II. ZERO TEMPERATURE TWO-LEVEL MEDIUM

In the case of a two-level medium with thickness \( L \), the transmittivity is

\[ B_n(\Delta) = \exp[i\chi(\Delta + n\Omega)kL/2], \]  

(S13)

with

\[ \chi(\Delta) = -3\pi \rho \Gamma / [k^3(\Delta + i\Gamma/2)]. \]  

(S14)

\( \rho \) the number density of atoms in the medium. We define

\[ b = \text{Im}\{\chi\}kL, \]  

(S15)

as the optical depth (OD), and,

\[ \phi = \text{Re}\{\chi\}kL/2, \]  

(S16)

as the optical phase shift due to the index of refraction of the two-level ensemble. The OD at resonance \( b_0 \) is defined by

\[ b_0 = \frac{6\pi \rho L}{k^2}. \]  

(S17)

The symmetric property of the susceptibility gives rise to the following relation for the transmittivity,

\[ B_n(\Delta) = B_{-n}^*(-\Delta). \]  

(S18)

Thus, for the two-level case, we find that the in-phase and in-quadrature components are both odd functions of \( \Delta \).

A. Case of conventional band-resolved FM spectroscopy

In the conventional band-resolved FM spectroscopy (\( \Omega \gg \Gamma \)), the modulation index \( \beta \) is small. Thus, one only needs to consider the beat note between the carrier and the first sidebands. The demodulated signal becomes

\[ I_d(\Delta) = iI_0J_1 \left\{ B_0^*(\Delta)B_1(\Delta) - B_0(\Delta)B_{-1}^*(\Delta) \right\}. \]  

(S19)

1. Small OD limit

In the limit of low OD \((b_0 \ll 1)\), we get \( B_{\pm 1} \approx 1 \) and \( B_0 \approx 1 - b_0/2 + i\phi \). The demodulated signal becomes

\[ I_d(\Delta) = I_P(\Delta) = 2I_0J_0J_1\phi, \]

\[ I_Q(\Delta) = 0. \]  

(S20)

The demodulated signal is non-zero only for the in-phase component, and has a dispersive profile suitable to generate an error signal for frequency stabilization of a laser.

2. Slope of the demodulated signals

Here, we derive the general expression for the slope of the demodulated signal [see Eq. (S19)] when the carrier is at resonance. We find

\[ B_0^*(\Delta)B_1(\Delta) - B_0(\Delta)B_{-1}^*(\Delta) \approx [B_0^*(\Delta) - B_0(\Delta)]. \]  

(S21)

Its derivative, evaluated at \( \Delta = 0 \), is given by

\[ \frac{d}{d\Delta} [B_0^*(\Delta) - B_0(\Delta)] \bigg|_{\Delta=0} = \frac{2i}{\Gamma} b_0 e^{-b_0/2}. \]  

(S22)

with \( b_0 = 6\pi \rho L / k^2 \) for a two-level medium.

The on-resonance slope of the demodulated signal is given by

\[ S_d \equiv \frac{dI_d}{d\Delta} \bigg|_{\Delta=0} = -2I_0J_0J_1b_0 e^{-b_0/2} \Gamma^{-1}, \]  

(S23)

resulting in Eq. (7) of the paper.
B. Case of $\beta = 2.4$

In the case of $\beta = 2.4$, as a first approximation, we consider only the first and the second sidebands. The in-phase and in-quadrature components become

$$I_P(\Delta) = I_0 J_1 J_2 \text{Im} \left\{ B_1(\Delta) B_2^*(\Delta) - B_{-1}(\Delta) B_{-2}(\Delta) \right\},$$
$$I_Q(\Delta) = I_0 J_1 J_2 \text{Re} \left\{ B_1(\Delta) B_2^*(\Delta) - B_{-1}(\Delta) B_{-2}(\Delta) \right\}. \quad (S24)$$

In complex notations, we have

$$I_\delta(\Delta) = iI_0 J_1 J_2 \left\{ B_1(\Delta) B_2(\Delta) - B_{-1}(\Delta) B_{-2}^*(\Delta) \right\}. \quad (S25)$$

Consider now the following expression

$$B_{\pm 1} B_{\pm 2}^* = \exp \left\{ -\frac{b_0}{2} \frac{\Gamma^2}{4(\Delta \pm \Omega)^2} \right\} \exp \left\{ -\frac{b_0}{2} \frac{\Gamma^2}{4(\Delta \pm 2\Omega)^2} \right\} \exp \left\{ -i\frac{b_0}{2} \frac{\Gamma}{2(\Delta \pm \Omega)} \right\} \exp \left\{ i\frac{b_0}{2} \frac{\Gamma}{2(\Delta \pm 2\Omega)} \right\}. \quad (S28)$$

Its derivative with respect to $\Delta$, and subsequent evaluation at $\Delta = 0$, is given by

$$\frac{d}{d\Delta} B_{\pm 1} B_{\pm 2}^* \big|_{\Delta=0} \approx iB_{\pm 1}(0) B_{\pm 2}^*(0) b_0 \frac{3\Gamma}{\Omega} \frac{1}{16\Omega}. \quad (S29)$$

Since $\Omega/\Gamma \gg 1$, we keep only the first order terms in $\Gamma/\Omega$. Therefore, we have

$$\frac{d}{d\Delta} \left[ B_1^* B_2 - B_{-1}^* B_{-2} \right] \big|_{\Delta=0} = -\frac{3i}{2} b_1 \exp (-5b_1/8 + i\phi_1/2) \Gamma^{-1}. \quad (S30)$$

We denote the OD and the optical phase shift at the position of the first sidebands to be $b_1 = b_0 \Gamma^2/(4\Omega^2)$ and $\phi_1 = b_0 \Gamma/(4\Omega)$, respectively. When the carrier component is at resonance, the slope of the demodulated signal is then given by

$$S_d = \frac{3}{2} I_0 J_1 J_2 b_1 \exp \left( -\frac{5}{8} b_1 + \frac{i}{2} \phi_1 \right) \Gamma^{-1}, \quad (S31)$$

leading to Eq. (8) of the paper.

III. DC TRANSMISSION AND DEMODULATED SIGNALS FOR CESIUM D2 LINE

A. Experimental DC transmission signals

The transmission from the cesium vapor cell passes through a beam splitter [see Fig. 2(a) in the paper], where $96\%$ of the power sent to a fast detector for frequency demodulation. The rest is sent to a detector to record the corresponding DC transmission curve. Some examples of the experimental DC transmission curves are shown in Fig. S1.

![Figure S1. Experimentally measured DC transmission curves at various vapor temperatures. Here, $\Omega = 706.8 \text{MHz} = 135.9\Gamma$.](image-url)

Since $\beta$ is close to 2.4, the carrier component has a small amplitude. For a medium with small OD, the sidebands are located at the tails of the absorption window, where the absorption is low. Therefore, a large fraction of the light is transmitted when the carrier frequency is at resonance. At larger OD, the absorption at spectrum center increases due to the widening absorption window.
B. Experimental demodulated signals

Some examples of the experimentally measured demodulated signals are shown in Fig. S2, for various vapor temperatures. The experimentally measured curves are plotted in blue, while the theoretical curves are plotted in red. In the first two columns, we plot the \( I_P \) and \( I_Q \) components of the demodulated signals. These components are obtained by applying a rotation to \( I_d \) [see Eq. (S12)], such that the rotated in-quadrature component, \( I_Q' \), has a zero slope at the spectrum center (see Section III D for determination of the spectrum center). In the third and fourth columns, we plot the magnitude and the phase of the demodulated signals. As the vapor temperature increases, the demodulated signals become more complicated, as evidenced by the increasing oscillations in the magnitude, and the rapid change in the phase of the demodulated signals.

C. Model for the transmittivity

For a cesium vapor of temperature \( T \) and thermal velocity \( \bar{v} \), we have the following transmittivity at the vicinity of the D2 line

\[
B(\Delta) = \exp \left[ -\frac{b_0}{2} \sqrt{\frac{\pi}{8k\bar{v}}} \sum_{F' = 3}^{5} S_{F'F} w \left( \frac{\Delta - \delta_{F'} + i\Gamma/2}{\sqrt{2k\bar{v}}} \right) \right],
\]

(S32)

where \( S_{F'F} \) is the transition strength factor. They take the values \( S_{4F'} = 7/72, 7/24 \) and \( 11/18 \), for \( F' = 3, 4 \) and \( 5 \) respectively [1]. The detuning \( \Delta \) is referred from the \( F = 4 \rightarrow F' = 5 \) transition. The two other relevant hyperfine excited states are detuned from the \( F' = 5 \) level by \( \delta_{F'} \). In this case, \( \delta_{F'} = -452.4, -251.1 \) and \( 0 \) MHz, for \( F' = 3, 4 \) and \( 5 \) respectively [1]. The function \( w(z) \), with a complex parameter \( z \), is the Faddeeva function. It is defined by \( w(z) = \exp(-z^2)\text{erfc}(-iz) \) [2]. We assume that the intensity of each sideband is low enough such that any saturation and optical pumping effects can be neglected. This transmittivity function is then used in Eq. (S9) to calculate the demodulated signals.

The expressions of the absorption cross sections for the D lines of alkali atoms, are found in Ref. [3]. Using the expression for the D2 line, we can write \( b_0 \) in terms of the atomic density \( \rho \),

\[
b_0 = \frac{18\pi L\rho}{(2I + 1)k^2}, \quad (S33)
\]

where \( I = 7/2 \) is the nuclear spin of cesium atoms.

The atomic density is then related to the vapor pressure \( P_v \) and vapor temperature \( T \),

\[
\rho = 133.323 \frac{P_v}{k_B T}. \quad (S34)
\]

In the above expression, \( T \) is specified in Kelvin and \( P_v \) in Torr. The vapor pressure of cesium is further related to its temperature [4],

\[
\log_{10} P_v = 2.881 + 4.711 - \frac{3999}{T}, \quad T < 301.64K,
\]

\[
\log_{10} P_v = 2.881 + 4.165 - \frac{3830}{T}, \quad T > 301.64K. \quad (S35)
\]

Eqs. (S34) and (S35) together link the temperature to \( b_0 \). Thus, in fitting our model to the experimental results, we do not have to set both \( b_0 \) and \( T \) as free parameters, since having one as a free parameter is already sufficient.

D. Determination of the spectrum center

To characterize the frequency sensitivity of the FM spectroscopy, we have to first identify the spectrum center \( \Delta_c \). This is especially important at large OD where there are multiple minima in the demodulated signal (see Fig. S3). In Fig. S3(a), we show the theoretical predictions for all minima located within the frequency range of \( -50 \Gamma \) to \( 0 \), as a function of \( b_1 \). Here, we assume a modulation frequency of \( \Omega/\Gamma = 135.9 \), corresponding to the experimental value. The range of \( b_1 \) value corresponds to temperatures ranging between 15 °C and 88 °C. We note that the positions of different minima changes as \( b_1 \) varies. The difficulty in identifying the spectrum center can be avoided with larger OD and modulation frequency. As shown in Fig. S3(b), the minima corresponding to \( \Delta_c \) remains unchanged as \( b_1 \) varies, and thus can be easily identified.

In Fig. S3, for each minimum identified, we also indicate its value of the demodulated signal slope, according to the color scales located on the right side of the plots.

E. Fit to the experimental data

Both the DC transmission and the two components of the demodulated signals are fitted with theoretically calculated spectra that take into account the three allowed transitions in the D2 line [see Eq. (S32)]. We fit only in the detuning range of \( -200 \leq \Delta/\Gamma_0 \leq 200 \), where \( \Gamma_0 \) denotes the natural linewidth of the transition.

The fits are used to extract information on the homogeneous linewidth of the resonance. To do so, we first perform a fit with \( \Gamma = \Gamma_0 \). We then repeat the fit for different values in the range of \( 0.1 \leq \Gamma/\Gamma_0 \leq 10 \). We then plot the residual sum of squares (RSS) of the fits, as a function of \( \Gamma/\Gamma_0 \). The RSS is calculated using

\[
\text{RSS} = \sum_i \left[ f(x_i) - y_i \right]^2, \quad (S36)
\]

where the summation is over all the data points, with \( y_i \) the experimentally measured points and \( f(x_i) \) the predicted value for the independent variable \( x_i \) [see Fig. 4(a) in the paper]. When the model is correctly accounting for the observations, the minimum point of the RSS gives
Figure S2. The demodulated signals at various vapor temperatures. The first column and second column shows the $I'_P$ and the $I'_Q$ components (see text for more details). The third column and the fourth column the magnitude of the demodulated signal, $I_D$, and phase of the demodulated signal, $\phi_D$. The blue curves are the experimental results and the red curves are the theoretical predictions including the three allowed transitions of cesium D2 line from the $F = 4$ ground state. The vapor temperatures indicated here are the temperatures obtained from the fits (see Section III E), which agree well with direct measurements of the temperatures on the setup.
us the homogeneous linewidth as measured by the large OD FM-spectroscopy.

In the following, we discuss individually the fits to the transmission spectra and to the demodulated spectra. Finally, we also describe the simultaneous fit performed on both the transmission spectra and the demodulated spectra.

1. Fit to the transmission spectra

For each fixed value of $\Gamma$, we let $T$ and $\beta$ be free parameters. We note that since $b_0$ is related to $T$, as discussed in Section III C, it is not set as a free parameter. The values of $\beta$ are constrained into an interval corresponding to observed variation of the EOM modulation index due to thermal effects. The DC transmission signal is first normalized by the transmission measurements at the two extreme ends of the frequency scan, before being fitted to the following expression,

$$A \sum_{n=0}^{5} J_n^2(\beta)|B_n(\Delta)|^2,$$

where $A$ is a free fitting parameter constrained to be close to 1.

The large OD FM-spectroscopy essential probes the tails of the resonance. Here the relevant parameter to describe the transmission spectrum is given by the product $b_0\Gamma^2$. So, $b_0$ (and therefore $T$) and $\Gamma$ are not completely independent parameters in describing the DC transmission spectrum. Thus, when varying the value of $\Gamma$ for the transmission spectra fits, the initial guess of $T$ has to be suitably chosen to ensure faster convergence to the solution. In the fits, we choose the initial guess of $T$ such that the product $b_0\Gamma^2$ is close to the value at $\Gamma = \Gamma_0$.

2. Fit to the demodulated signals

The temperature resulting from the fit of the DC transmission is then taken as the initial guess for the fit to the demodulated signals. Since the phase shift of the demodulated signal is unknown, an additional phase factor $\phi_\tau$ is added to Eq. (S9). The real and imaginary parts of the following expression are then fitted to the two experimentally measured demodulation signal components.

$$BI_d(\Delta)\exp(i\phi_\tau)$$

where $I_d(\Delta)$ is taken from Eq. (S9), and calculated for $0 \leq n \leq 5$.

$B$ is a scaling factor that has to be determined. We first perform the fit with $B$ being a free parameter, at $\Gamma = \Gamma_0$. The values of $T$ and $\beta$ from this fit is used to calculate the transmission spectrum in absence of any frequency modulation. From this spectrum, we then calculate the value of $b_1$ at each vapor temperature. We then compare the slope of the experimental data to the theoretical prediction [Fig. 3(b) in the paper]. The best agreement between the experimental data and the theoretical curve is achieved at $B = 0.69$. This sets the value of $B$ for subsequent fits, when $\Gamma/\Gamma_0$ varying in the range of 0.1 to 10. The value $B = 0.69$ corresponds to a gain of 1.3 kV/W for the fast detector. This gain is independently calibrated to be 1.1 kV/W, using an intensity modulated laser beam. The two methods that measure the gain of the fast detector agree to within 17%.

Similar to the case of the transmission spectra, the initial guess of $T$ has to be appropriately chosen. Here, we find, instead, that $b_0\Gamma$ is the relevant parameter, since the main oscillating feature of the demodulated signal depends predominantly on the phase shift experienced by the different sidebands. Hence, the initial guess of $T$ is chosen to keep the product $b_0\Gamma$ close to the value at $\Gamma = \Gamma_0$.

3. Simultaneous fit of the experimental spectra

To improve on the sensitivity of the fit to the linewidth $\Gamma$, a simultaneous fit of the experimental spectra (DC transmission and demodulated signals) are performed. Here, we take advantage of the different scaling behaviors
of \( b_0 \) with \( \Gamma \), i.e., constant \( b_0 \Gamma^2 \) for the DC transmission and constant \( b_0 \Gamma \) for the demodulated spectra. The RSS value from such a fit is divided by three, in order to have a fair comparison with the RSS value of the fit only to the transmission spectra.

4. Curvature at the minima of RSS curves

To calculate the curvature at the minima of the RSS curves [see for example Fig. 4(a) in the paper], we focus on small range of \( \Gamma \) values around the RSS minima. In the case of fits to only the transmission spectra, we fit the RSS curve within this small range, to the following fit function

\[
A \{ \exp[-B(\Gamma/\Gamma_0 - x_0)] + B(\Gamma/\Gamma_0 - x_0) \} + C,
\]

where \( A, B \) and \( C \) are the fitting parameters. The curvature is found to be \( AB^2 \). Here, \( x_0 \) gives the homogeneous linewidth of the D2 line, in units of \( \Gamma_0 \). In the case where the demodulated spectra is also included in the fits, we fit the RSS curve around the minimum, to a quadratic function. The coefficient of the second order term gives us directly the curvature.

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