High-Resolution Spectroscopy of Hyperfine Structure Using Phase-Correlated Four-Wave Mixing

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We have obtained high-resolution spectra of hyperfine transitions in an excited state ($^1D_2$) of Pr^{3+}:$YAlO_3$ using a novel four-wave-mixing technique. Subkilohertz resolution is obtained. The hyperfine transition line shapes are determined unambiguously, revealing an interesting effect of mutual-flip interaction between the $|m=\pm\frac{1}{2}\rangle$ hyperfine states of the Pr ions and the host nuclear spins. The necessary conditions for obtaining laser-jitter-independent resolution in inhomogeneously broadened samples are discussed.

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Obtaining higher frequency resolution is one of the central goals of spectroscopy, and tremendous effort has gone into the development of stable, narrow-bandwidth light sources to achieve this goal. In many spectroscopic studies, however, it is the relative, not the absolute, frequency resolution that matters, as, for example, in the measurement of hyperfine structures within electronic levels. In such studies, a stable, narrow-bandwidth laser is only an advantage, not a necessity. In fact, it is known that in some multiwave-mixing spectroscopies, under certain conditions, the relative frequency resolution can be totally independent of laser frequency jitter (fluctuation) [1-4].

One example is near-degenerate four-wave-mixing (FWM) spectroscopy. It has been demonstrated that if all three excitation fields in FWM are from a single laser (and thus phase correlated) and the medium's absorption width is broader than the laser width, resonances much narrower than the laser width [2-4] can be obtained. Superficially, the condition that the absorption be broader than the laser width is only to ensure that the laser always resonantly interacts with the medium. More subtly, it also ensures that the medium's response time is shorter than the phase-correlation time of the laser, so that the polarizations in the medium follow the phase fluctuation of the excitation fields instantaneously. Only then can the phase noise of the laser be completely canceled out. This is the scenario for homogeneously broadened media. With inhomogeneous broadened media, however, the response time is given by the phase memory time (optical dephasing time T_2), which in many low-temperature solids can be significantly longer than the phase-correlation time of commercial cw lasers (0.1 ms vs 1 μs). In this case, the polarizations in the medium cannot follow the phase fluctuation of the excitation fields instantaneously. As a result, the FWM spectrum is no longer independent of laser jitter. On the other hand, the hyperfine transition dephasing time in a solid is usually correlated to the optical dephasing time [5]. To obtain sharp hyperfine resonances, one is confined to samples with a large T_2. This dilemma is thus a serious obstacle to general application of the FWM technique.

We present here a study of hyperfine structures of a $^1D_2$ level in a crystalline system of Pr^{3+}:$YAlO_3$ using a novel time-resolved FWM spectroscopy. We show that jitter-free resolution can be achieved in inhomogeneous broadened samples by temporally selecting the instantaneous response part of the FWM signal. The hyperfine splitting in our sample ($\sim$1 MHz) is comparable to the width of the cw dye laser used in the experiment and thus cannot be (and has never been) resolved with conventional saturation spectroscopy (spectral hole burning). Being free of laser jitter, our technique clearly resolved the hyperfine resonances with widths of $\sim$6 kHz and achieved uncertainties of $\sim$0.1 kHz, thus significantly improving the accuracy of the hyperfine splitting measurements in this system. The high resolution also allows unambiguous determination of the hyperfine transition line shapes, which reveals an unexpected phenomenon, i.e., the mutual-flip interaction between the $|m=\pm\frac{1}{2}\rangle$ hyperfine states of the Pr ions and the host nuclear spins. This interesting effect has never been observed in previous studies of this type of system.

We begin with a brief discussion about phase-correlated FWM. Consider a FWM experiment where three excitation laser fields are on resonance with an inhomogeneously broadened two-level optical transition. The bandwidth of the laser is finite but narrower than the inhomogeneous width. Along one of the phase-matched directions, $\mathbf{k}_s=-\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3$, the signal is in the form of $E_s\sim E_1^* E_2 E_3$, where $\mathbf{k}_i$ and E_i denote the wave vector and E field of the ith laser beam. E_1 and E_2 are square pulses from a single laser, which is turned on during $(0,t_p)$, and travel through nearly identical optical paths, so the phase noise $\phi_1(t)=\phi_2(t)=\phi(t)$. E_2 is frequency shifted from E_1 by a stable low-frequency source, $\omega_1-\omega_2=\Delta$. E_3 is a time-delayed short pulse, $E_3\sim\delta(t-T_w)$, with $T_w>t_p$. The intensity of the laser is assumed to be stable. By solving the equation of motion of a two-level density matrix (third-order perturbation) [6] and averaging over the inhomogeneous broadening, we can show that

$$E_s(\Delta,t)\sim\int_{T_w-t_p}^{2T_w-t}dt'\exp[-i\Delta(T_w-t')-t'/T_b]\exp[-i\Delta\phi(T_w-t',t-T_w)-2(t-T_w)/T_2]\,, \quad (1)$$

where T_b is the excited-state lifetime, $\Delta\phi=\phi(T_w-t')-\phi(T_w-t'-(t-T_w))$, and T_2 is the off-diagonal element relaxation time and hence the (optical) dephasing time. It is evident that, if detected at $t=T_w$, the signal as a function of Δ (i.e., the FWM spectrum) is independent of the laser phase noise $\phi(t')$. The frequency resolution is limited only by the stability of the low-frequency source.

For multilevel excitations, Eq. (1) is slightly modified. It can be shown that if a long-lived "bottleneck" level exists, the factor $\exp[-t'/T_b]$ in Eq. (1) is simply replaced by $(2-\eta)\exp[-t'/T_b]+\eta\exp[-t'/T_c]$, where η is the probability for the excited state to relax to the bottleneck and T_c is the lifetime of the bottleneck. When the frequency shift Δ is on resonance with a hyperfine transition width the excited electronic level, $\Delta\sim\omega_{m'm}$, one can show that the integrand is multiplied by a two-point correlation function:

$$g(t')=\left\langle \exp\left[-i\int_0^{t'}\omega_{m'm}\,dt''\right]\right\rangle .$$

By a conventional definition, the Fourier transform of $g(t)$, $G(\Delta)=F[g(t)]$, is the resonant absorption spectrum of the hyperfine transition [7]. In this case, we can rewrite Eq. (1) as

$$E_s(\Delta,t=T_w)\sim\int d\Delta' G(\Delta-\Delta')\tilde{L}(\Delta'),$$
$$\tilde{L}(\Delta)\sim\int_{T_w-t_p}^{T_w}dt\exp[-i\Delta(T_w-t)-t/T_b]. \tag{2}$$

Similar to the two-level resonance described by Eq. (1), the hyperfine spectrum is also independent of the laser phase noise.

The necessary conditions for achieving laser-jitter-free resolution are thus as follows: (1) E_1 and E_2 are from a single source and have similar optical paths so that they are phase correlated. (2) The optical absorption is wider than the laser bandwidth so that the frequency jitter does not reduce the total time of the laser-medium interaction. (3) Signal detection is instantaneous with the probe field E_3. For homogeneously broadened media, only the first two conditions are required. Condition (2) ensures that the response time (the inverse of the absorption width) of the medium is shorter than the laser phase-correlation time, which is equivalent to condition (3). The response time of inhomogeneously broadened media, on the other hand, is given by the phase memory time (dephasing time) T_2, which in practical situations is usually longer than the laser phase-correlation time. Thus, condition (3) must be explicitly stated for inhomogeneously broadened media.

Experimentally, the condition for the instantaneous detection can be achieved by shortening the optical dephasing time T_2. In gaseous-phase spectroscopy, this can be done by introducing buffer gases to increase the collision rate. In solids, a higher temperature readily results in a shorter T_2. When instantaneous detection is achieved in this manner, the real-time analysis here becomes equivalent to the analysis of the steady-state measurements used by the other authors [1–4]. In practice, however, this approach can seriously affect the hyperfine spectrum, especially in the case of solids. A phonon-induced transition to an adjacent electronic level, which is the main mechanism for the reduction of T_2 in most solid-state systems, would totally destroy the phase coherence between the hyperfine levels and hence broaden the hyperfine transitions. To avoid this undesirable situation, we used a new technique that combines the best features of time-resolved and steady-state FWM spectroscopy, achieving laser-jitter-free resolution by temporally resolving the instantaneous response part ($t\simeq T_w$) of the FWM signal.

The experiment was performed on a 0.1% Pr^{3+}:$YAlO_3$ crystal. The sample is immersed in the liquid-helium cryostat at 2.0 K. The optical transition (610.7 nm) is between the lowest Stark components of the $^3H_4$ and $^1D_2$ states of the trivalent Pr ions, which have a nuclear moment $I=\frac{5}{2}$. The optical dephasing time is $T_2=35$ μs [5]. The hyperfine structure under investigation is within the excited- (electronic-) state level ($^1D_2$). The average value of the electronic angular momentum for this level is zero, $\langle\mathbf{J}\rangle=0$. The hyperfine splitting is due to the second-order $\mathbf{J}\cdot\mathbf{I}$ coupling and the coupling between the nuclear quadrupole and the crystal-field gradient [7]. The hyperfine levels are doubly degenerate ($E_m=E_{-m}$, where m denotes the magnetic number of the nuclear moment), and thus the hyperfine transitions $|m\rangle\leftrightarrow|m'\rangle$ and $|-m\rangle\leftrightarrow|-m'\rangle$ are indistinguishable. The frequency splittings are only about 1 MHz and are barely resolvable with conventional saturation spectroscopy (spectral hole burning) [5]. Hyperfine splitting values obtained with other commonly used techniques, such as photon-echo modulation and Raman heterodyne spectroscopy, are all instrument limited [5]. Intrinsic line shapes of the hyperfine transitions have never been obtained.

The cw output of a Coherent 699-21 ring dye laser (nominal short-time width $\lesssim 1$ MHz) is modulated by two separate acousto-optical modulators (AOM) to produce the pulse sequence and the relative frequency shift described above. A double-pass geometry is used to compensate for the beam displacement associated with the frequency shift. The rf source for AOM1 (E_1 and E_3) is a crystal oscillator. A frequency synthesizer (HP 8656B) is used as the variable rf source to drive AOM2 (E_2). The output of the crystal oscillator is monitored by a frequency counter (HP 5343A) and is fed back to the synthesizer through a computer to correct for the slow frequency drift. The combined uncertainty in the relative frequency shift is 2×10 Hz. As discussed, E_1 and E_2 are square pulses, and E_3 is a short pulse (500 ns, which is short compared to the phase-correlation time of the laser).

A "boxcar" geometry [8] is used for the FWM. The laser beams propagate (nearly) along the c axis. E_2 and E_s are polarized perpendicular to E_1 and E_3 so the scattering from E_3 can be rejected by a polarizer. The

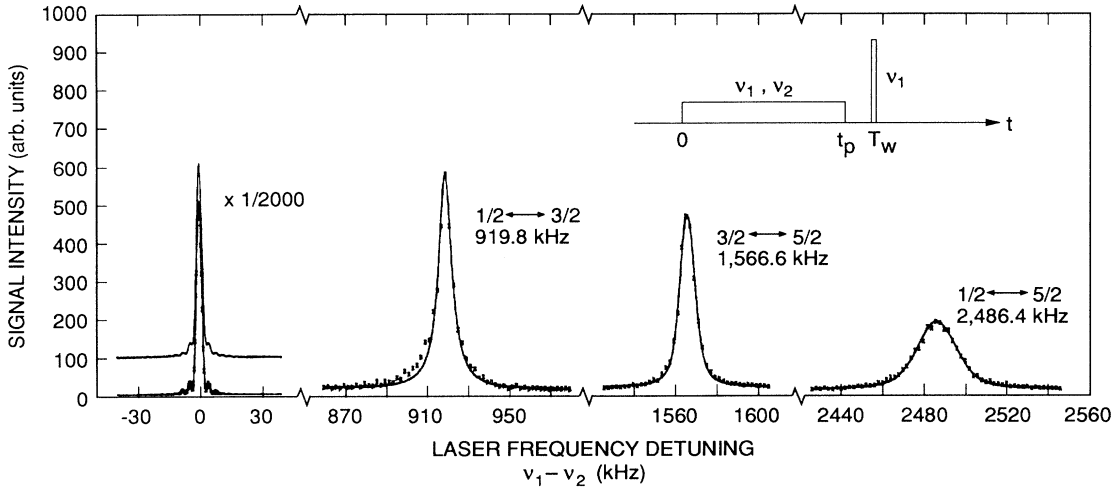

FIG. 1. FWM signal as a function of frequency detuning. The offset solid curve at $\nu_1 - \nu_2 \sim 0$ is the calculated instrument resolution. The solid curves at the hyperfine resonances are calculations based on Eq. (2). The hyperfine absorption spectra $G(\Delta)$ are assumed to be Lorentzian for the $|\pm\frac{1}{2}\rangle \leftrightarrow |\pm\frac{3}{2}\rangle$ transition, and Gaussian for the $|\pm\frac{3}{2}\rangle \leftrightarrow |\pm\frac{5}{2}\rangle$ and $|\pm\frac{1}{2}\rangle \leftrightarrow |\pm\frac{5}{2}\rangle$ transitions. The excitation pulse sequence is shown in the right corner of the figure.

signal is detected along $\mathbf{k}_s = -\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3$. A gated integrator is used to select detection time. For instantaneous detection, the gate of the integrator is set to overlap in time with E_3.

The FWM signal intensity as a function of frequency detuning is shown in Fig. 1. The experimental conditions for taking this set of spectra are $t_p = 300$ μs and $T_w = 301$ μs. The laser intensities are (10 mW)/(0.4 mm^2), (1 mW)/(0.4 mm^2), and (40 mW)/(0.4 mm^2) for E_1, E_2, and E_3, respectively. Each data point corresponds to an average of 100 shots. The solid curves at the hyperfine resonances are calculations based on Eq. (2). The offset solid curve at $\nu_1 - \nu_2 \sim 0$ is calculated using Eq. (1) and represents the instrument resolution. The lifetime of the excited state ($^1D_2$) used in the calculation is the measured value $T_b = 175$ μs. The hyperfine absorption spectra $G(\Delta)$ are assumed to be Lorentzian for the $|\pm\frac{1}{2}\rangle \leftrightarrow |\pm\frac{3}{2}\rangle$ transition ($\nu_0 = 919.8 \pm 0.1$ kHz, FWHM $= 5.8 \pm 0.1$ kHz), and Gaussian for the $|\pm\frac{3}{2}\rangle \leftrightarrow |\pm\frac{5}{2}\rangle$ ($\nu_0 = 1566.6 \pm 0.1$ kHz, FWHM $= 6.7 \pm 0.1$ kHz) and $|\pm\frac{1}{2}\rangle \leftrightarrow |\pm\frac{5}{2}\rangle$ ($\nu_0 = 2486.4 \pm 0.3$ kHz, FWHM $= 18.0 \pm 0.3$ kHz) transitions. These values represent improvements in accuracy of several orders of magnitude compared with previous all-optical measurements and more than 1 order of magnitude compared with rf-optical double-resonance measurements [5].

When the gate of the integrator is increased to 2 μs, the spectra are noticeably broadened, which confirms the importance of the instantaneous detection. No sign of power broadening is observed. It is worthwhile noting that, to a first-order approximation, the broad laser bandwidth used here causes the saturation level to increase by a factor of (laser width)/(natural width) ~ 500. Power broadening is thus much less of a problem than would be predicted by normal theoretical analysis, where an ultrastable laser source is usually a presumption. The applied laser intensity (and the total laser energy) in our measurement is limited by the optical pumping (persistent hole burning), which depletes the resonant ions and hence reduces the FWM signal. To minimize this effect, the laser frequency was scanned slowly over the inhomogeneous absorption profile (300 MHz) during the signal averaging process.

It is beyond the scope of this paper to discuss in detail the mechanisms for the broadening of the hyperfine transitions. However, the most distinctive feature of our data, the Lorentzian shape of the $|\pm\frac{1}{2}\rangle \leftrightarrow |\pm\frac{3}{2}\rangle$ transition (Fig. 2) as compared to the Gaussian shapes of the other transitions, has a simple physical explanation. In previous studies, it was commonly assumed that all hyperfine transitions in rare-earth-doped crystals are inhomogeneously broadened and hence have near-Gaussian line shapes. The Lorentzian shape of the $|\pm\frac{1}{2}\rangle \leftrightarrow |\pm\frac{3}{2}\rangle$ transition is the result of the finite lifetime of the $|\pm\frac{1}{2}\rangle$ states. Because $|+\frac{1}{2}\rangle$ and $|-\frac{1}{2}\rangle$ are degenerate, the Pr ions in these states interact resonantly with the host nuclear spins (Al spins) through the spin-flip coupling term, $I^+(\mathrm{Pr})I^-(\mathrm{Al})$, which results in transitions between the two states, $|+\frac{1}{2}\rangle \leftrightarrow |-\frac{1}{2}\rangle$ (transitions between the other $|\pm m\rangle$ states are inhibited by the selection rule $\Delta m = \pm 1$). If the broadening of the $|\pm\frac{1}{2}\rangle \leftrightarrow |\pm\frac{3}{2}\rangle$ transition ($\Delta\nu = 5.8$ kHz) is solely determined by this lifetime effect, we would predict a transition rate of $2\pi\Delta\nu = (27\ \mu\mathrm{s})^{-1}$. In comparison, an estimate using the "golden rule" gives a value of $\sim(40\ \mu\mathrm{s})^{-1}$.

In conclusion, we have shown that instantaneous response of the medium is a key condition for laser-jitter-independent frequency resolution in phase-corre-

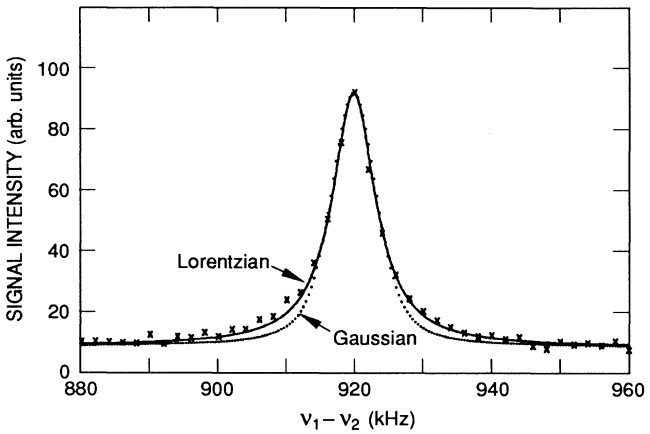

FIG. 2. FWM spectrum of the $|\pm\frac{1}{2}\rangle \leftrightarrow |\pm\frac{3}{2}\rangle$ hyperfine transition. Experimental condition: same as Fig. 1 except $t_p = 1.0$ ms. The solid curve is the calculated spectrum obtained using a Lorentzian line shape with $\nu_0 = 919.8$ kHz and FWHM = 5.8 kHz. The dotted curve is that obtained using a Gaussian line shape with the same parameters.

lated FWM and that it can be achieved by temporally resolving the FWM signal. We have applied this technique to obtain high-resolution spectra of hyperfine transitions in the $^1D_2$ state of Pr^{3+}:$YAlO_3$. Our results not only significantly improve the numerical accuracy of the hyperfine splitting in this system but also reveal an important effect of the mutual-flip interaction between the $|m = \pm\frac{1}{2}\rangle$ hyperfine states of the Pr ions and the host nuclear spins. This technique should be useful for studying narrow energy splittings in solids, both for the splitting induced by the hyperfine interaction studies here and for splittings by other interaction mechanisms.

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