

optically pump and probe the alkali polarization. A magnetic field in the z direction rotates the alkali polarization away from the direction of light propagation, and correspondingly, the absorption of the light increases. In order to avoid interference from low-frequency noise, a modulation of the z component of the magnetic field is applied at a frequency  $\nu_{mod}=1.8$  kHz, with amplitude similar to the width of the alkali Zeeman resonance (about 15 nT in the vapor cell used here). The z component of the magnetic field due to the sample leads to modulation of the transmitted light at the first harmonic of the modulation frequency, which is monitored with the lock-in amplifier **132**. FIG. **2A** shows the response of the magnetometer to a small oscillating test field as a function of frequency. FIG. **2B** shows the sensitivity of the magnetometer (the sharp peaks are for calibration) after normalizing the measured noise and calibration signals by the frequency response of the magnetometer, yielding a noise floor of about 200 fT/√Hz, flat from about 3 Hz to 300 Hz.

**[0043]** Data presented in this work was acquired as follows: Fluid polarized by the Halbach array **108** flows into the detection volume **110**, and at  $t=0$ , flow is halted and a pulse of DC magnetic field is applied in the y direction with magnitude  $B_1$  and duration  $T_p$ . This rotates the proton and  $^{13}\text{C}$  spins by different angles due to the different magnetogyric ratios, placing the spin system into a superposition of eigenstates of the J-coupling Hamiltonian, Eq. (1). The ensuing quantum beats lead to a time-dependent magnetization, the z component of which is detected by the atomic magnetometer. The transfer of the sample from high field to zero field is adiabatic as no quantum beats are observed without application of an excitation pulse. Adiabatic transfer results in equilibration of the spin-temperature parameters of the two species via the J-coupling interaction, the initial condition for simulations presented below.

**[0044]** Experiments were performed with  $^{13}\text{C}$  enriched methanol ( $^{13}\text{CH}_3\text{—OH}$ ), ethanol 1 ( $^{12}\text{CH}_3\text{—}^{13}\text{CH}_2\text{—OH}$ ), and ethanol 2 ( $^{13}\text{CH}_3\text{—}^{12}\text{CH}_2\text{—OH}$ ) obtained from Cambridge Isotope Laboratories. Methanol and ethanol 2 data were acquired with no further sample preparation. Ethanol 1 data were acquired following several freeze-thaw cycles under vacuum to help remove any dissolved gases, e.g.  $\text{O}_2$ , however the linewidth and longitudinal relaxation time was similar for ethanol 1 and ethanol 2.

**[0045]** Results and Discussion:

**[0046]** Measurements on methanol,  $^{13}\text{CH}_3\text{OH}$ , are presented in FIGS. **3A** and **3B** for a pulse area  $\alpha=B_1T_p(\gamma_H+\gamma_C)=2.4$  rad ( $T_p=0.66$  ms). The signal in the time domain after averaging 11 transients is shown in FIG. **3A**. There is a large, slowly decaying component of the signal due to the relaxation of static components of the total magnetization, as well as a smaller, high frequency component due to scalar coupling. Overlaying the data is a decaying exponential with time constant  $T_1=2.2$  s. In displaying these data, the decaying exponential was first subtracted, filtered the remaining signal with a pass band between 120 and 300 Hz and then added the decaying exponential to the filtered data. This eliminates transients at the beginning and end of the data set due to the digital filter. The Fourier transform of the signal is shown in FIG. **3B** after correcting for the finite bandwidth of the magnetometer, revealing a simple structure consisting of two peaks (offsets inserted for visual clarity). This spectrum is in agreement with the discussion of  $^{13}\text{CH}_3$  given above, assuming that the homo- and heteronuclear coupling of the OH group are averaged to zero under rapid chemical exchange.

Independently fitting the low- and high-frequency portions of the data to complex Lorentzians yields central frequencies  $\nu_1=140.60$  Hz and  $\nu_2=281.09$  Hz with linewidths (half-width at half-maximum)  $\Delta\nu_1=0.10$  Hz and  $\Delta\nu_2=0.17$  Hz. These values are in agreement with the value found in the literature of  $J_{HC}=140.6$  Hz for methanol.

**[0047]** The amplitudes of the low- and high-frequency peaks as a function of pulse area are shown by triangles and squares, respectively in FIG. **4A**. Using the formalism discussed above, one can show that if the polarized part of the density matrix prior to the excitation pulse is of the form

$$\rho = \beta \sum_j I_{j,z},$$

the amplitude of the two resonances is given by

$$A_1=2(\gamma_C\gamma_H)\sin(B_1T_p(\gamma_H+\gamma_C))\sin(B_1T_p(\gamma_H-\gamma_C)), A_2=5A_1/4 \quad (\text{Eq. 4})$$

**[0048]** The lines overlying the data are theoretical predictions, in agreement with the data. This dependence can be understood as follows: Following the pulse, the protons and  $^{13}\text{C}$  nuclei precess around the total angular momentum F, and hence the time dependent magnetization is produced in a direction transverse to F. The projection of the transverse component of F along the z axis following the pulse is modulated according to  $\sin B_1T_p(\gamma_H+\gamma_C)$ , and the amplitude of the time dependent part of the magnetization transverse to F is determined by the phase difference accrued by protons and  $^{13}\text{C}$  nuclei during the pulse, yielding the final  $\sin B_1T_p(\gamma_H-\gamma_C)$  factor in Eq. 4.

**[0049]** In FIG. **3A**, there is a slowly decaying exponential with a time constant  $T_1=2.2$  s, and on top of this, a smaller, oscillating signal due to coupling of the  $^{13}\text{C}$  with the protons. The real and imaginary parts of the spectrum are represented in FIG. **3B** by the upper and lower traces, respectively. The low-frequency and high-frequency peaks correspond to the coupling of the  $^{13}\text{C}$  nucleus with the doublet and quadruplet states of proton angular momentum, respectively.

**[0050]** In order to determine the stability of the J-coupling measurement, a series of 100 transients were acquired following the application of a pulse with area  $\alpha=2.4$  rad, the first maximum of the response in FIG. **4A**. The raw data were binned into sets of ten, averaged, Fourier transformed, and fit to complex Lorentzians. The position of the low-(triangles) and high-(squares) frequency peaks are shown as a function of bin number in FIG. **4B**. The mean frequencies of each peak are indicated by the solid lines overlying the data with  $\nu_1=140.566(4)$  Hz and  $\nu_2=281.082(3)$  Hz. As mentioned above, these values appear to be in agreement with the value found in the literature, however, these data deviate slightly from the  $^{13}\text{CH}_3$  model discussed above because  $\nu_2/2$  differs from  $\nu_1$  by about 25 mHz. It is suspected that this small shift is the result of residual coupling to the OH group, and simulation indicates that it would require a coupling of only 0.4 Hz to produce a shift of this magnitude and sign. The statistical uncertainties in these measurements are orders of magnitude smaller than the range of frequencies associated with J-couplings, providing a sensitive probe for subtle differences in chemical structure.

**[0051]** In FIG. **4A**, triangles and squares show the dependence of the amplitude of the low- and high-frequency resonances in  $^{13}\text{C}$  enriched methanol on pulse area, respectively. The solid lines overlying the data are theoretical predictions