

and A. Llor, Z. Olejniczak, A. Pines, Coherent isotropic averaging in zero field NMR: 1. general theory and icosahedral sequences, *J. Chem. Phys.* 103 (1995) 3966-3981).

[0035] Nuclear magnetic resonance is a powerful analytical tool for determination of molecular structure and properties. There are generally a number of terms in the NMR Hamiltonian that can be used for understanding molecular structure, including the Zeeman interaction, dipole-dipole coupling, quadrupole coupling, and scalar coupling discussed here. While operation at zero field eliminates the Zeeman interaction, all other terms in the NMR Hamiltonian remain. The present invention demonstrates that it is possible to detect the scalar coupling interaction in a zero field environment. Scalar couplings yield information about the presence of covalent bonds, bond angle, torsion, and strength. As a more “blunt instrument”, they could be used as a marker to determine if a reaction has occurred, for example, to see if a drug molecule has bound to the appropriate receptor. If used to monitor the products of a reaction, catalyzed, by enzymes or microreactors, J-couplings could be used to optimize the performance of the catalyst.

[0036] The present invention could be widely used in both pure research environments, as well as industry. For example; the invention could be used to evaluate the effectiveness of an experimental catalyst by monitoring covalent bonds in the product of the reaction. The pharmaceutical industry could be potentially interested in this invention because it may aid in drug discovery programs by providing a tool to monitor whether a drug molecule has bound to a receptor. More generally, the present invention may find application in a chemical production facility by monitoring concentrations of reactants, products, or un-wanted by-products, where such process information may be used to adjust process parameters.

[0037] The present invention may also find applications in security monitoring, for example, in the detection of liquid hydrocarbons, which often have more energy per unit mass than TNT. While an existing technique for detection of solid explosive compounds employs NQR (nuclear quadrupole resonance) spectroscopy, it does not work for liquids. One particular security monitoring application may be in an airport screening machine that detects liquid explosives by finding a recognized J-coupling spectra.

[0038] At zero magnetic field, the Hamiltonian for a network of spins coupled through scalar interactions is

$$H_J = \hbar \sum_{j,k} J_{jk} I_{j,z} I_{k,z} \quad (\text{Eq. 1})$$

where the sum extends over all distinct spin pairs and J_{jk} is the J-coupling parameter for spins j and k. The observable in the present invention is the z component of the magnetization of the sample (see Experimental section below),

$$M_z(t) = \hbar n \text{Tr} \left(\rho(t) \sum_j \gamma_j I_{j,z} \right) \quad (\text{Eq. 2})$$

where n is the number density of molecules, γ_j is the magnetogyric ratio of the j-th spin, and $\rho(t)$ is the density matrix. The temporal evolution of an arbitrary system of spins can be determined by diagonalizing the Hamiltonian to find the eigenstates $|\phi_a\rangle$ and eigenvalues E_a , and expressing the ini-

tial density matrix as a sum of the operators $|\phi_a\rangle\langle\phi_b|$, each of which evolves as $e^{i\omega_{ab}t}$, where $\omega_{ab} = (E_a - E_b)/\hbar$.

[0039] Because $I_{j,z}$ are vector operators with magnetic quantum number zero, observable coherences are those between states that differ by one quantum of total angular momentum F, $|\Delta F| = 1$ with $\Delta M_F = 0$. This selection rule can be used for prediction of the positions of peaks and for interpretation of spectra. For instance, consider the case of $^{13}\text{CH}_N$, where the J-coupling J_{CH} between all N heteronuclear pairs is identical. Since the protons are all equivalent, the homonuclear J-couplings can be ignored (see ref 2). Denoting the total proton spin by K and the ^{13}C spin by S, Eq. (1) can be rewritten $H_J = \hbar J_{HC} K \cdot S$, which has eigenstates $|F^2, K^2, S^2, F_z\rangle$ with eigenvalues

$$E_{F,K} = \hbar \frac{J_{HC}}{2} [F(F+1) - K(K+1) - S(S+1)]. \quad (\text{Eq. 3})$$

[0040] The selection rules above yield the observable quantum-beat frequencies $\omega_K = (E_{K+1/2,K} - E_{K-1/2,K})/\hbar = J_{HC}(K+1/2)$ for $K \geq 1/2$. For the methyl group, $^{13}\text{CH}_3$, two lines are expected, one at J_{HC} and another at $2 J_{HC}$, corresponding to coupling of the ^{13}C nucleus with the proton doublet or quadruplet states. For the methylene group, $^{13}\text{CH}_2$, a single line at $3 J_{HC}/2$ is expected due to coupling with the proton triplet state. In more complicated molecules, homonuclear couplings or higher-order effects of heteronuclear couplings can result in a splitting of the lines—however, the positions of the multiplets can be determined by the above argument.

EXPERIMENTAL

[0041] A schematic of the zero-field spectrometer **100** is shown in FIG. 1. The detection volume **110** and the vapor cell **112** of the optical-atomic magnetometer are housed inside a set of magnetic shields **114** and coils **120** to create a zero-field environment to a level of 0.1 nT. A syringe pump **102** cycles fluid analyte between the polarization volume **106** and the 80- μL detection volume **110** via a 50-cm long tube with inner diameter of 250 μm . The prepolarizing volume is placed in a compact (5 cm \times 5 cm \times 10 cm) 1.8-T Halbach array **108**. A pressurized reservoir **126** aids refilling the syringe on the refill cycle. The flow rate is 50 $\mu\text{L/s}$, yielding an average fluid velocity of 100 cm/s and transit time of 0.5 s from magnet to detection region (small compared to the longitudinal relaxation rate of the samples measured here). A solenoid **124** provides a “guiding field” in transit from the ambient laboratory field to zero field to ensure that the initial magnetization points towards the atomic magnetometer.

[0042] The central component of the magnetometer is a vapor cell, with inner dimensions 2.7 mm \times 1.8 mm \times 1 mm, containing ^{87}Rb and 1200 Torr of N_2 buffer gas, fabricated using the techniques described by Knappe et al in *Optics Letters*. The atomic magnetometer operates in the spin-exchange relaxation-free (SERF) regime (see, I. K. Kominis, T. W. Kornack, J. C. Allred, M. V. Romalis, A sub-femtoTesla multichannel atomic magnetometer, *Nature* 422 (2003) 596-599), in which relaxation of the alkali polarization due to spin-exchange collisions is eliminated. As described by Shah et al. in *Nature Photonics*, a single circularly polarized laser beam is used here, which is tuned to the center of the pressure broadened Rb D1 transition, propagating in the x direction, to