

ble spin quantum numbers of the operator \mathbf{k} describing the sum of the equivalent proton spins, and $s = 1/2$ is the spin quantum number associated with the operator \mathbf{s} , representing the ^{13}C spin. To first order in B_z , eigenstates are those of the unperturbed Hamiltonian, and Zeeman shifts of the eigenvalues can be read from the diagonal matrix elements of the Zeeman perturbation. One finds:

$$\begin{aligned} \Delta E(f, k, m_f) &= -\langle f m_f | B_z (\gamma_h k_z + \gamma_c s_z) | f m_f \rangle \\ &= -B_z \sum_{m_k, m_s} \langle k s m_k m_s | f m_f \rangle^2 (\gamma_h m_k + \gamma_c m_s). \end{aligned} \quad (2)$$

Here γ_h and γ_c are the proton and ^{13}C gyromagnetic ratios, and $\langle k s m_k m_s | f m \rangle$ are the Clebsch-Gordan coefficients. The observable in our experiment is the total x magnetization, $M_x(t) \propto \text{Tr} \rho(t) \sum_j I_{jx} \gamma_j$, where $\rho(t)$ is the time dependent density matrix. Writing I_{jx} in terms of the raising and lowering operators, we obtain selection rules for observable coherences: $\Delta f = 0, \pm 1$ and $\Delta m_f = \pm 1$, valid in the limit where $|\gamma_j B| \ll |J|$. In the case at hand with N equivalent protons, there is an additional selection rule, $\Delta k = 0$, since, in the absence of chemical shifts, the Hamiltonian commutes with \mathbf{k}^2 .

Experimentally, we examine the case of $N = 1$ and $N = 3$. In the former case, $k = 1/2$, the zero-field levels are a singlet with $f = 0$ and a triplet with $f = 1$. In the presence of a small magnetic field, the singlet level is unperturbed, while the triplet levels split, as shown by the manifolds on the left of Fig. 1(a). In the following, ν_{f, m_f}^{f', m'_f} denotes the frequency of transitions between the states $|f, m_f\rangle$ and $|f', m'_f\rangle$. Employing Eq. (2) and the selection rules, one finds a single line for transitions with $\Delta f = 0$ between states with $f = 1$, and a doublet for transitions with $\Delta f = \pm 1$ between states with $f = 1$ and $f = 0$:

$$\nu_{1, m_f}^{1, m_f \pm 1} = B_z (\gamma_h + \gamma_c) / 2, \quad (3)$$

$$\nu_{0, 0}^{1, \pm 1} = J \pm B_z (\gamma_h + \gamma_c) / 2. \quad (4)$$

For the case of $N = 3$, k is either $1/2$ or $3/2$. The $k = 1/2$ transition frequencies are given by Eq. (4). The $k = 3/2$ manifolds are shown on the right of Fig. 1(a), and coherences between $|f = 1, m_f\rangle$ and $|f = 2, m_f \pm 1\rangle$ occur at frequencies given by

$$\nu_{1, m_f}^{2, m_f \pm 1} = 2J + m_f \frac{B_z}{4} (-7\gamma_h + 6\gamma_c) \pm \frac{B_z}{4} (3\gamma_h + \gamma_c). \quad (5)$$

There are two additional transitions for states with $k = 3/2$ with $\Delta f = 0$ that occur near zero frequency,

$$\nu_{2, m_f}^{2, m_f \pm 1} = (3\gamma_h + \gamma_c) B_z / 4; k = 3/2, \quad (6)$$

$$\nu_{1, m_f}^{1, m_f \pm 1} = (5\gamma_h - \gamma_c) B_z / 4; k = 3/2. \quad (7)$$

Equations. (3)-(7) constitute a set of eleven transitions, three appearing near zero frequency, two near J , and six