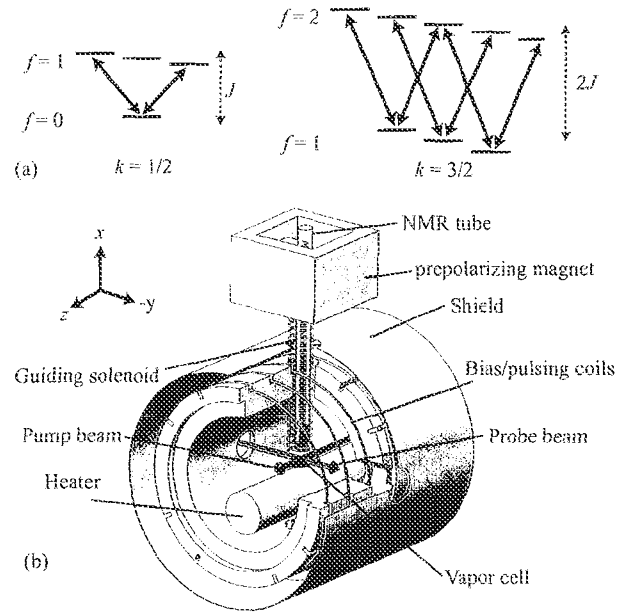

FIG. 1: (color online) (a) Energy levels for a $^{13}CH_3$ group. Energy levels for a ^{13}CH group are given by the manifold on the left. (b) *Experimental setup for near-zero-field spectroscopy*, described in the text.

near $2J$, representing the NZF NMR spectrum of a $^{13}CH_3$ group. These calculations are discussed in more depth in the Supplementary Information, and in Ref. [17].

We now make two observations: (1) Even in more complex molecules with additional non-equivalent spins, the zero-field eigenstates are also those of $\mathbf{f}^2$ and f_z. Therefore, the NZF splitting patterns can be used to identify the angular momenta of the states involved in the zero-field transitions: Transitions between levels with $f=0$ and 1 will produce doublets, transitions between levels with $f=1$ and 2 will produce a multiplet with six lines, and so on. (2) The selection rules presented here break down as the magnetic field becomes large enough to produce significant mixing of the zero-field eigenstates. Reference [17] shows theoretically that the maximum number of lines for a $^{13}CH_N$ group is $(N+1)^2$, most clearly visible when $|(\gamma_h+\gamma_c)B_z| \approx J$.

Experiments were performed using an apparatus similar to that of Refs. [14, 16] and depicted in Fig. 1. Samples (typically ≈ 200 μL) were contained in a 5 mm NMR tube, and pneumatically shuttled between a 1.8 T prepolarizing magnet and a magnetically shielded enclosure, housing a microfabricated ^{87}Rb vapor cell, the central component of the atomic magnetometer. The cell is optically pumped by z-directed, circularly polarized laser light, tuned to the center of the D1 transition, and probed by y-directed, linearly polarized light, tuned about 100 GHz to the blue of the D1 transition. Optical rotation of the probe light is monitored by a balanced polarimeter. Bias fields and DC pulses of magnetic field,