



FIG. 2: Spectra for ^{13}C labeled formic acid, H^{13}COOH , in the indicated magnetic fields. The spectra are the result of averaging eight transients. The inset shows the splitting of the two lines centered about J as a function of magnetic field.

used to excite NMR spin coherences, are applied via a set of coils. At zero field, the magnetometer is primarily sensitive to fields in the x direction with noise floor of about $40 - 50 \text{ fT}/\sqrt{\text{Hz}}$. As the bias field is increased, the magnetometer response moves to higher frequencies, compromising the low-frequency sensitivity by about a factor of 5 for $B_z = 3 \text{ mG}$. To maintain a quantization axis during transit of the sample, a solenoid provides a “guiding” field. The guiding field is turned off suddenly prior to acquisition of data, and a pulse applied in the z -direction with area such that the proton spins rotate through $\approx 4\pi$ and the carbon spins rotate through $\approx \pi$ (about $480 \mu\text{s}$), maximizing the amplitude of zero-field signals.

ZF and NZF spectra for formic acid (H^{13}COOH) are shown in Fig. 2. The ZF spectrum consists of a single line at $J = 222 \text{ Hz}$, as well as a DC component, suppressed here for clarity. The NZF spectrum arising from the ^{13}CH group is as discussed above: a doublet with frequencies $J \pm B_z(\gamma_h + \gamma_c)/2$ and an additional line at $B_z(\gamma_h + \gamma_c)/2 \approx 4.7 \text{ Hz}$. The large peak at 7.5 Hz corresponds to the uncoupled OH group. The asymmetry in the doublet centered about J , reproduced by a full numerical calculation, is due to higher-order corrections to the eigenstates. The peaks are well described by Lorentzians, with half-width at half-maximum $\approx 0.1 \text{ Hz}$, and the locations of the peaks can be determined with an uncertainty of about 1 mHz . The inset shows the splitting of the line at J as a function of magnetic field, displaying a linear dependence. The slope is in agreement with that predicted by Eq. (4), $(\gamma_h + \gamma_c)$, at the level of about 0.1% .

To illustrate the case of a $^{13}\text{CH}_3$ system, ZF and NZF spectra for acetonitrile-2 ($^{13}\text{CH}_3\text{CN}$) are shown in Fig 3. For $B_z = 0$, the spectrum consists of a zero-frequency peak, a peak at J , and a peak at $2J$. Application of a magnetic field splits the zero-frequency peak into three lines, whose frequencies are given by Eqs. (3),(6), and (7). The smallest peak at 11.2 Hz corresponds to an