



## Zero-field nuclear magnetic resonance spectroscopy of viscous liquids



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## ABSTRACT

We report zero-field NMR measurements of a viscous organic liquid, ethylene glycol. Zero-field spectra were taken showing resolved scalar spin–spin coupling ( $J$ -coupling) for ethylene glycol at different temperatures and water contents. Molecular dynamics strongly affects the resonance linewidth, which closely follows viscosity. Quantum chemical calculations have been used to obtain the relative stability and coupling constants of all ethylene glycol conformers. The results show the potential of zero-field NMR as a probe of molecular structure and dynamics in a wide range of environments, including viscous fluids.

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## 1. Introduction

Recent developments in zero- and ultra-low-field (ZULF) NMR with superconducting quantum interference devices (SQUIDs) [1–3] and atomic magnetometers [4–7] open new possibilities for imaging and spectroscopy. In conventional NMR spectroscopy, chemical shifts and spin–spin couplings are utilized to distinguish molecular structures [8,9], where spin–spin couplings are treated as a first-order perturbation to the Zeeman energy. To obtain high sensitivity and resolution of chemical shifts, high magnetic fields are conventionally used, requiring expensive radio-frequency spectrometers and bulky superconducting magnets with cryogenic cooling. ZULF-NMR with atomic magnetometers utilizing alkali-atom vapor cells has enabled non-cryogenic, desktop spectroscopy [5–7]. While chemical shifts vanish at zero field, ZULF-NMR spectra are governed by indirect nuclear spin–spin couplings called scalar or  $J$ -couplings that depend on the electronic structure and geometry of the molecule [5,10]. In contrast to the chemical shift due to diamagnetic current of the occupied orbitals, the  $J$ -coupling is an indirect interaction between nuclear spins through second-order

hyperfine effects [8,9,11–13], and thus serves as a sensitive local probe of molecular geometry and electronic structure.

Until now, investigations of ZULF-NMR with atomic magnetometers have focused on low-viscosity liquids with simple molecular structures and weak intermolecular interactions [5–7], achieving half width at half maximum as low as  $\approx 0.01$  Hz [14–16] comparable to that of advanced high-field (HF) NMR. Many materials of practical interest – polymers or proteins, for example, feature significant van der Waals interactions and hydrogen bonds. Therefore, the ability to detect such interactions through their  $J$ -coupling spectra in ZULF-NMR is of significant importance. Compared to HF-NMR, ZULF-NMR may have advantages in resolution because of the absence of the static and dynamic broadening mechanisms inherent in the spectroscopy of chemical shifts. For a liquid sample, the linewidth of ZULF-NMR is governed by the dynamical width due to nuclear dipole fields and  $J$ -coupling [9]. However, the magnitude of  $J$ -couplings sensitively depends on the molecular conformation and interactions in a way that is not always straightforward to predict.

Here we use a model system,  $^{13}\text{C}_2$ -labeled ethylene glycol (EG,  $\text{HO}-^{13}\text{CH}_2-^{13}\text{CH}_2-\text{OH}$ ), featuring strong intermolecular hydrogen bonds. NMR has been utilized to investigate molecular dynamics [17,9,18] and conformational equilibria of polyalcohols [19–26]. Among ten non-equivalent isomers of EG with different dihedral

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angles in one C–C and two C–O torsion angles, theoretical calculations have shown that two *gauche* conformers with a C–C torsion angle at possible potential minima,  $60^\circ$  and  $300^\circ$ , are favorable rather than *trans* conformers with a torsion angle of  $180^\circ$  [27–35]. The two-bond  $J$ -couplings in  $^1\text{H}$  NMR measurements support the predominant *gauche* state [19–26]. However, NMR studies of EG have been usually made in solution states [19–26] possibly due to the broadening of NMR spectra in neat EG, and the effect of intermolecular hydrogen bonding between EG molecules for the conformations remains insufficiently explored.

In this paper, we study the effect of viscosity on ZULF- and HF-NMR spectra by controlling the viscosity through varying temperature and water content of EG solutions. We observe changes in ZULF-NMR spectra that are due to minute changes in  $J$ -couplings that can be attributed to intermolecular hydrogen bonding and molecular dynamics in bulk EG.

## 2. Experimental technique

The ZULF-NMR apparatus has been described previously in Ref. [7] and references therein. An EG sample pre-polarized in a permanent 2.0 T magnet situated outside the magnetic shield was shuttled to the zero-field region through a guiding coil. Because the low frequencies of ZULF-NMR preclude the use of inductive detection, NMR signals were detected with an atomic magnetometer incorporating a Rb vapor cell ( $^{87}\text{Rb}$  and 1300 torr  $\text{N}_2$ ) operating at  $180^\circ\text{C}$ . The alkali vapor was optically polarized with circularly polarized light tuned to the D1 transition. Magnetic field measurements were performed by continuously monitoring optical rotation of linearly polarized light, propagating in a direction perpendicular to the pump beam, tuned about 100 GHz away from the center of the pressure broadened D1 transition. Optical rotation of the probe beam was monitored by using a balanced polarimeter or by using a polarimetry scheme involving a quarter-wave plate/photoelastic modulator and a crossed polarizer. In the latter case, phase sensitive detection was used. ZULF-NMR transient signals were collected for 4–12 s following application of a  $\sim 1$  ms duration magnetic-field pulse to excite nuclear spin coherences. For the measurements presented here, 256 or fewer transients were averaged prior to Fourier transformation. The sample temperature was controlled by flowing hot air and monitored with a thermocouple.

NMR measurements were performed with bulk EG (1,2- $^{13}\text{C}$  ethanediol from Sigma Aldrich with 1–2% water content as measured by Karl-Fischer titration) and dilutions with distilled water in a 5 mm diameter Pyrex tube. The materials were used without further purification. The volume of EG was 100  $\mu\text{L}$  for the undiluted sample and 50  $\mu\text{L}$  for aqueous solutions. NMR tubes were sealed with parafilm to reduce evaporation and absorption of water. The spectra were obtained by Fourier transformation of the free-decay signals after cancellation of phase independent external noise (e.g., that from power lines) and subtraction of thermal-drift signals of the magnetometer. To obtain the linewidth and shift of spectral peaks, the ZULF spectra were fitted to a sum of Lorentzians.

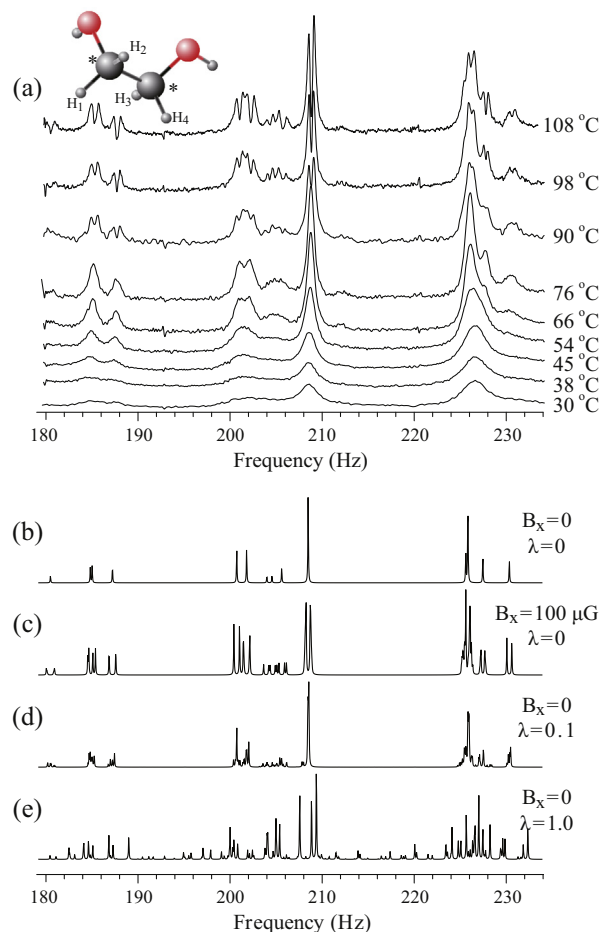
## 3. Computational method

The optimized structure of each of the ten conformers was obtained via energy minimization including second-order Møller–Plesset correlation energy corrections [36] and using a triple- $\zeta$  quality correlation-consistent basis set augmented with diffuse functions (MP2/aug-cc-pVTZ). Solvent reaction field of chloroform (dielectric constant  $\epsilon = 4.7$ ) and ethylene glycol ( $\epsilon = 37.7$ ) was included by means of the polarisable continuum model [37]. Electronic energies were corrected with the addition

of enthalpy and entropy corrections at 298 K to obtain the Gibbs free energies. Subsequent calculations of  $J$ -couplings, also in the presence of the solvent reaction field, were run using density functional theory with the BHandH functional [38] and the pcJ-2 basis set [39], which is specifically tailored for the calculation of spin–spin couplings. All contributions to  $J$  were included: the Fermi-contact, diamagnetic and paramagnetic spin–orbit and spin–dipole terms. All calculations were run with the Gaussian09 software package [38]. Following Ref. [40], we label each structure with three letters representing the HOCC, OCCO and CCOH dihedral angles. Lower case  $g$ ,  $g'$ ,  $t$  indicate values around  $+60^\circ$ ,  $-60^\circ$  and  $180^\circ$ , respectively, while uppercase  $G$  and  $T$  refer to the *gauche* or *trans* OCCO conformation, respectively. Figures are shown in Supporting Information. Degeneracy of the conformers was taken into account in the calculation of the population distribution and weighted average  $J$ -couplings.

## 4. Results and discussion

The thermal variations of internuclear interactions were studied by ZULF-NMR spectra of bulk ethylene glycol. Fig. 1 shows ZULF-NMR spectra at temperatures from 30 to  $108^\circ\text{C}$ . To understand



**Fig. 1.** (a) Temperature dependence of the ZULF-NMR spectrum of bulk  $^{13}\text{C}_2$ -ethylene glycol. The vertical axis is the Fourier transformed lock-in signal. The inset figure shows molecular structure of ethylene glycol (*gauche* conformer) where \* denotes  $^{13}\text{C}$ , small spheres: H atoms; intermediate spheres: O. (b) Simulation of  $76^\circ\text{C}$  spectrum without couplings to hydroxyl protons at zero magnetic field. (c) Spectral simulation without couplings to hydroxyl protons in the presence of a 100  $\mu\text{G}$  field. (d) Spectral simulation with couplings to hydroxyl protons scaled by  $\lambda = 0.1$  at zero magnetic field. (e) Spectral simulation including full couplings to hydroxyl protons ( $\lambda = 1$ ) at zero magnetic field. Simulated spectra are shown with narrow linewidth (extended relaxation time) in order to reveal fine structure.

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