

## Temperature Dependence of the Methyl Group Dynamics of Ethanol in a Glycerol-Water Environment

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### Introduction

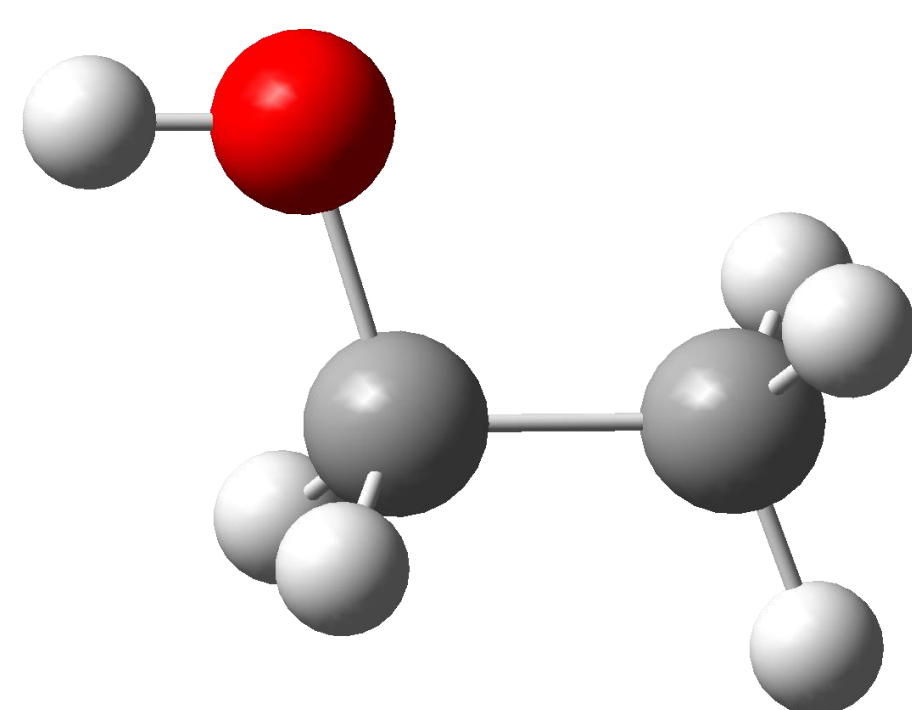


Fig. 1: Structure of Ethanol.

When investigating the structure of biomolecules using solid state NMR spectroscopy, the sensitivity and site-specificity play an important role. Recently, it was shown that an enhancement of both factors is possible with the combination of SCREAM-DNP (Specific Cross Relaxation Enhancement by Active Motions under Dynamic Nuclear Polarization) and Rotational Resonance in a publication of Biedenbänder et al. [1]. In order to obtain a better understanding of the mechanistic details of the polarization transfer, it is important to know the methyl-group dynamics. Here, we use ethanol in a glycerol-water environment as a model system to study these dynamics and their temperature dependence with molecular dynamics (MD) simulations and quantum chemical calculations.

### Simulation Methodology

MD simulations of 55 ethanol molecules, 723 water molecules and 222 glycerol molecules (mixture 1) and 222 ethanol molecules, 482 water molecules and 296 glycerol molecules (mixture 2) were performed under NPT conditions at  $p = 1$  bar for various temperatures. We employed the force field TIP4P/2005 [2] for water and OPLS-AA [3] for glycerol and ethanol. For both mixtures, simulations were performed with undeuterated as well as deuterated methyl groups; for mixture 2 additionally  $\frac{2}{3}$  undeuterated and  $\frac{1}{3}$  deuterated methyl groups.

### Vibrational Frequencies

In order to obtain the methyl group librational motions, the dihedral angle velocity autocorrelation function was calculated.

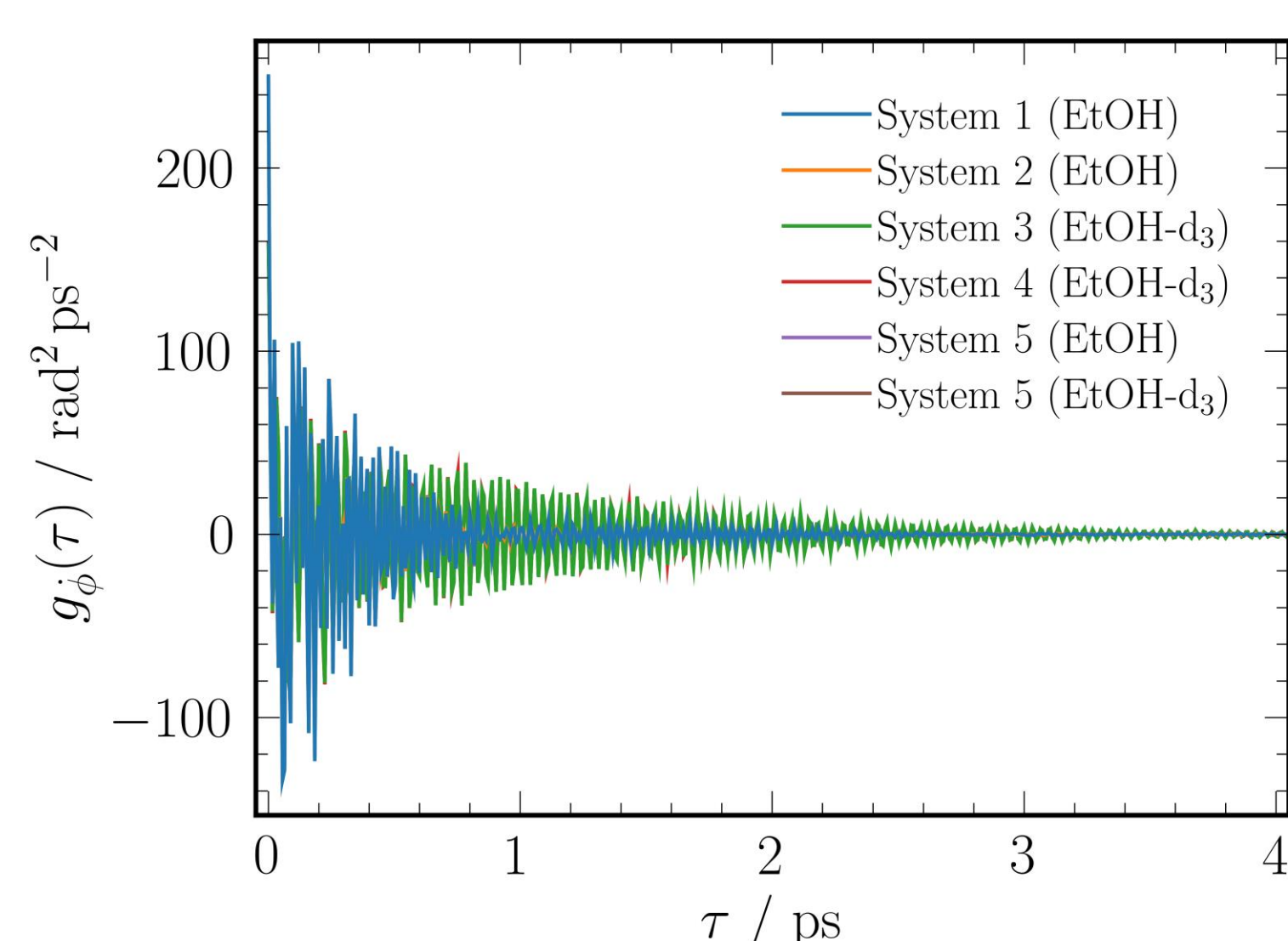


Fig. 2: Methyl group dihedral angle velocity autocorrelation function at  $T = 298$  K.

A frequency spectrum can then be obtained by FOURIER transforming this autocorrelation function. Additionally, *ab initio* calculations of ethanol with both undeuterated and deuterated methyl groups have been performed at the B3LYP/6-311G\*\* [4] level of theory.

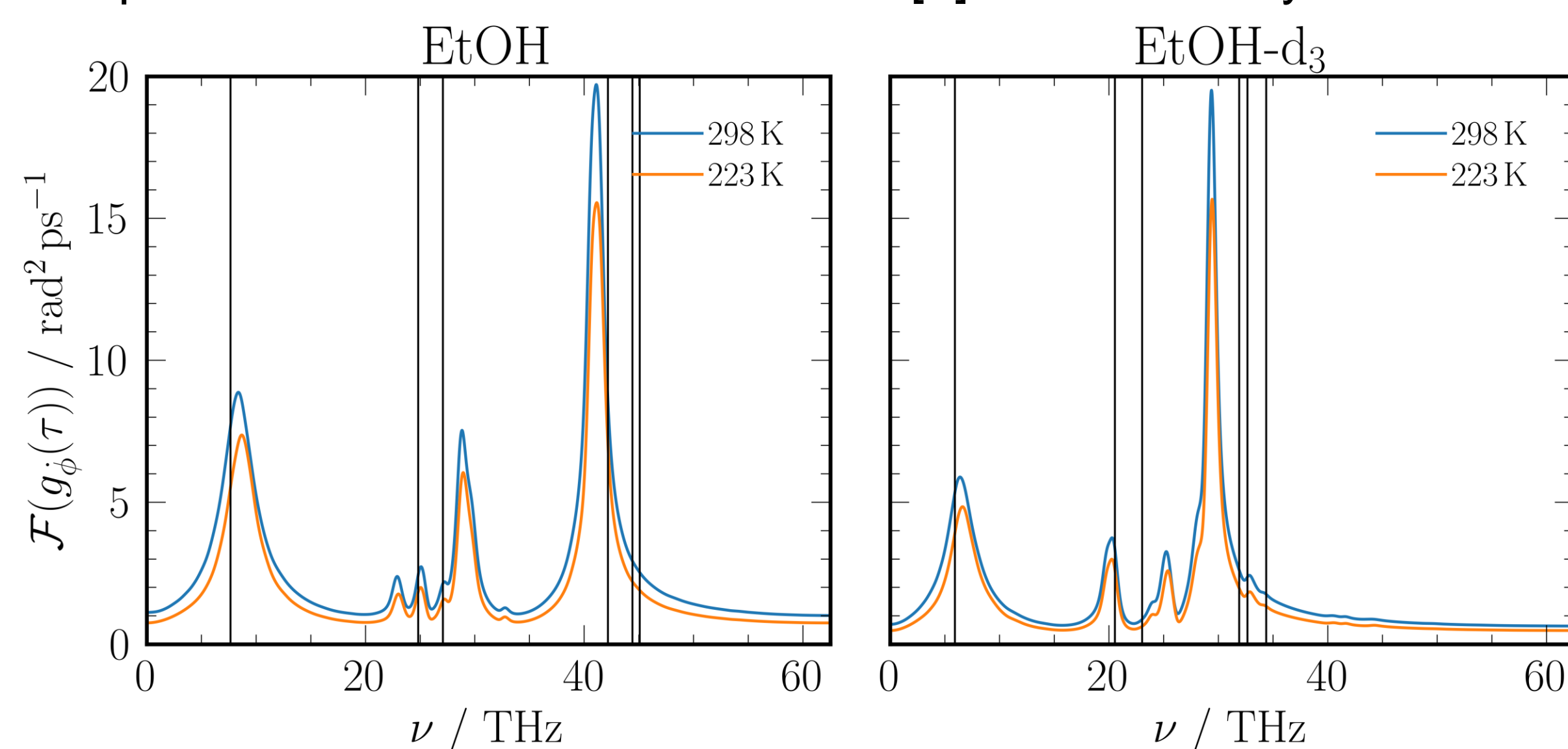


Fig. 3: Methyl group vibrational frequencies from MD simulations and *ab initio* calculations.

### Diffusion Coefficient Analogue

A quantity analogous to the diffusion coefficient can be calculated for the methyl group dihedral angle. For that, a dihedral angle trajectory is evaluated using the EINSTEIN approach.

$$D_\phi = \frac{1}{2} \lim_{t \rightarrow \infty} \frac{d}{dt} \langle \Delta \phi^2(t) \rangle$$

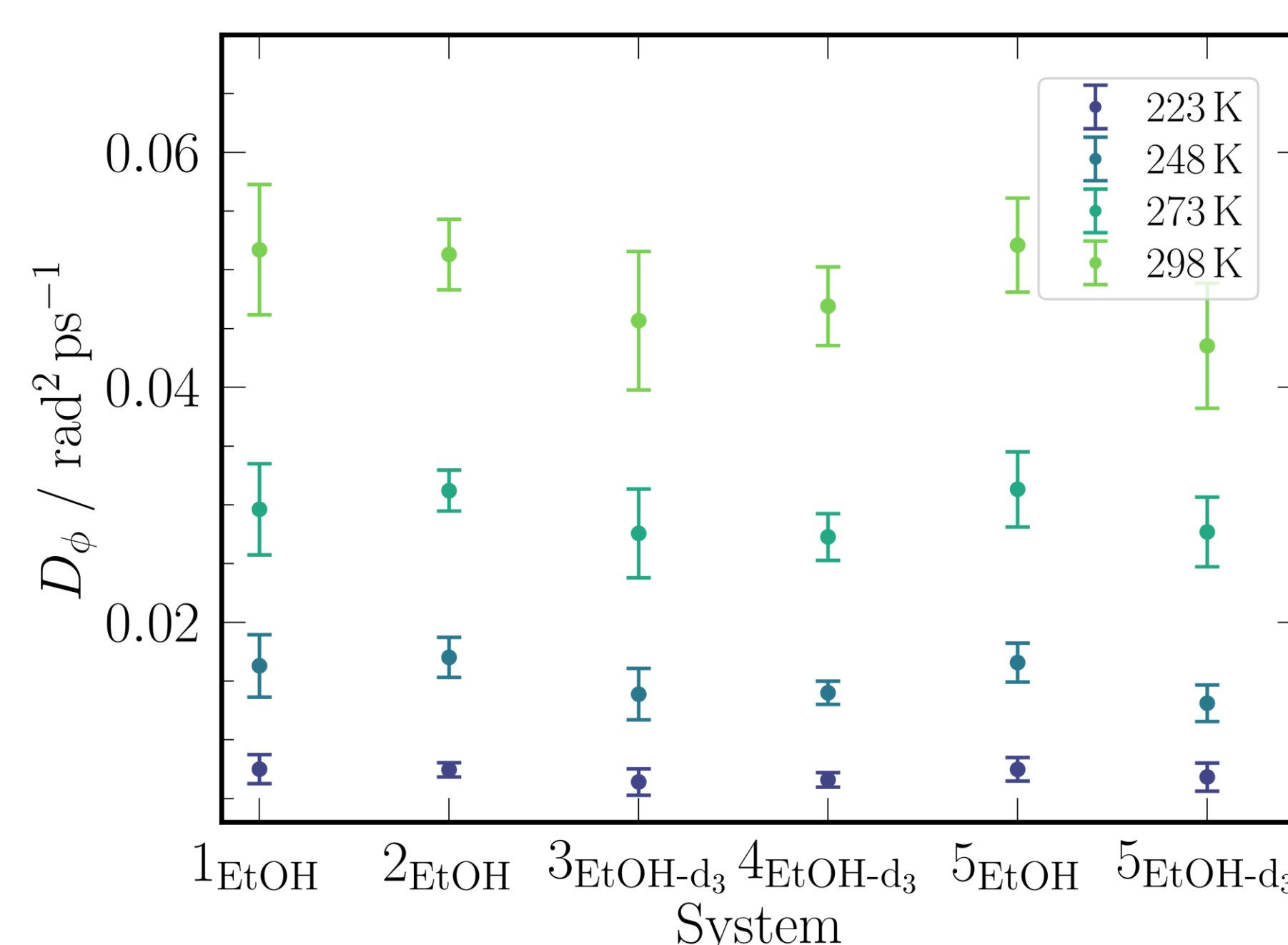


Fig. 4: Diffusion coefficient analogues of the methyl group dihedral angle of the ethanol mixtures at different temperatures.

The diffusion coefficient analogue can then be used to calculate the residence time of the methyl group using the following equation:

$$\tau_r = \frac{\langle l^2 \rangle}{2D_\phi} = \frac{(\frac{2}{3}\pi)^2}{2D_\phi}$$

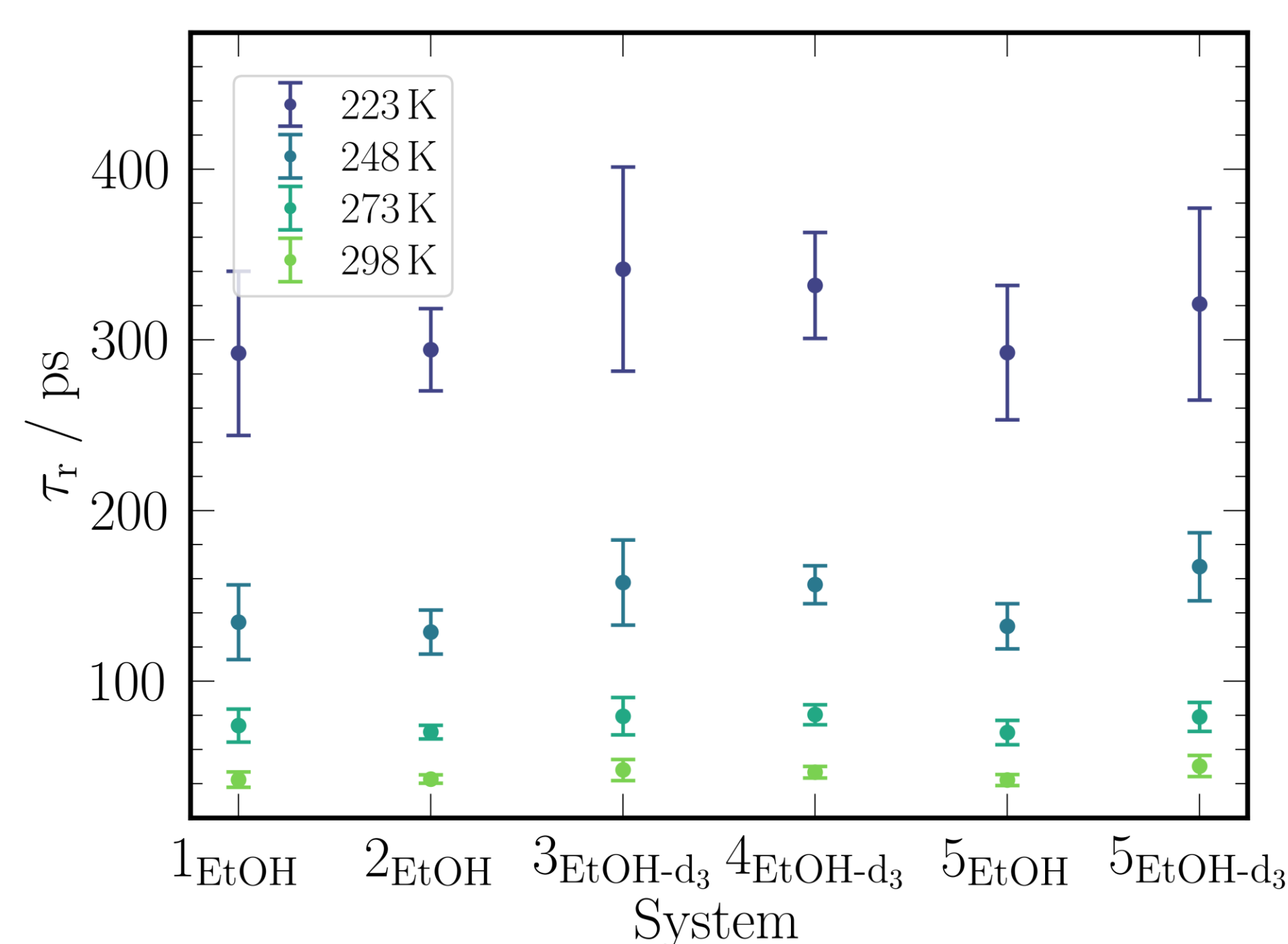


Fig. 5: Residence times of the methyl group dihedral angle of the ethanol mixtures at different temperatures.

### References

- [1] T. Biedenbänder, E. R. Bensons, and B. Corzilius, *ChemPhysChem* **2023**, *24*, e202300206.
- [2] J. L. F. Abascal, and C. Vega, *J. Chem. Phys.* **2005**, *123*, 234505.
- [3] W. L. Jorgensen, D. S. Maxwell, and J. Tirado-Rives, *J. Am. Chem. Soc.* **1996**, *118*, 11225–11236.
- [4] P. J. Stephens, F. J. Devlin, C. F. Chabalowski, and M. J. Frisch, *J. Chem. Phys.* **1993**, *98*, 11623–11627.

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