Supporting information for manuscript #: MOLLIQ-D-25-01407

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"Spectroscopic and complementary thermodynamic study
of liquid, supercooled, and glassy state of ethylene glycol"

The IR spectra of liquid EG were previously reported and no absorption band was found at 1653 cm^{-1} [References 31 and 33 in the main text]. However, the more recent publication [Reference 28 in the main text] reports such an absorption band, which was ascribed to a CH_2 scissoring that is active in the IR but not active in the Raman.

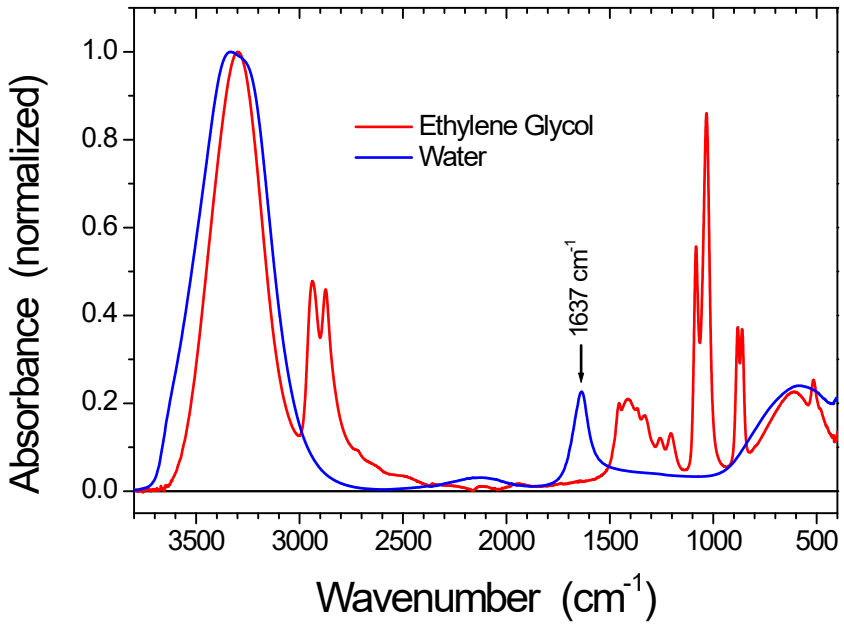

Figure S1. Comparison of the IR spectra of water and EG at room temperature.

We repeated the measurement using an anhydrous EG sample and compared the spectrum obtained to that of water (Figure S1.) No band was found at 1653 cm^{-1} in the EG spectrum, but a band at 1637 cm^{-1} is observed in the IR spectrum of water, possibly indicating an artefact in Reference 28 due to contamination of EG with water.

Our manuscript predominantly deals with the C-C-O bending mode in the EG Raman spectra of the liquid, supercooled and glassy states. Because of the discrepancies in the literature, it is pertinent to repeat the Raman spectroscopy measurements of the liquid and crystalline state of EG to ensure the accuracy of the wavenumbers and assignments of the modes studied in this and other works.

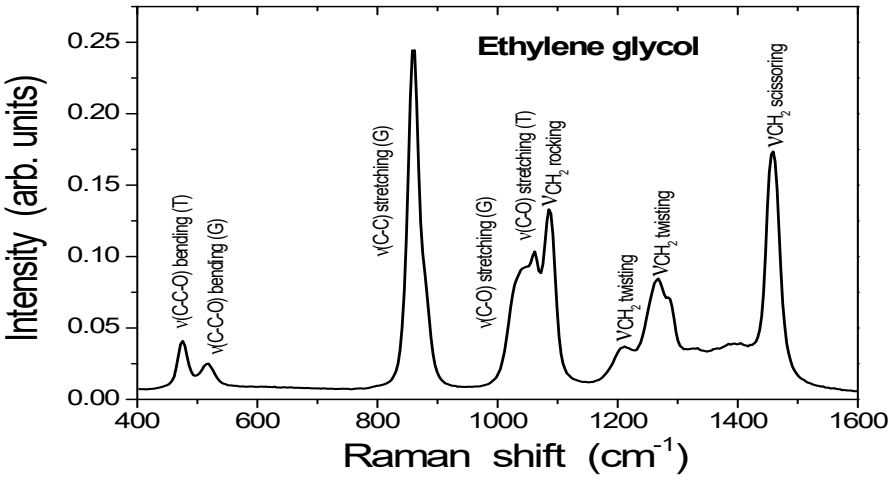

Figure S2A. Room temperature Raman spectrum of EG in the spectral range 400 – 1600 cm^{-1} with the peaks assigned according to the References in Tables S1 & S2.

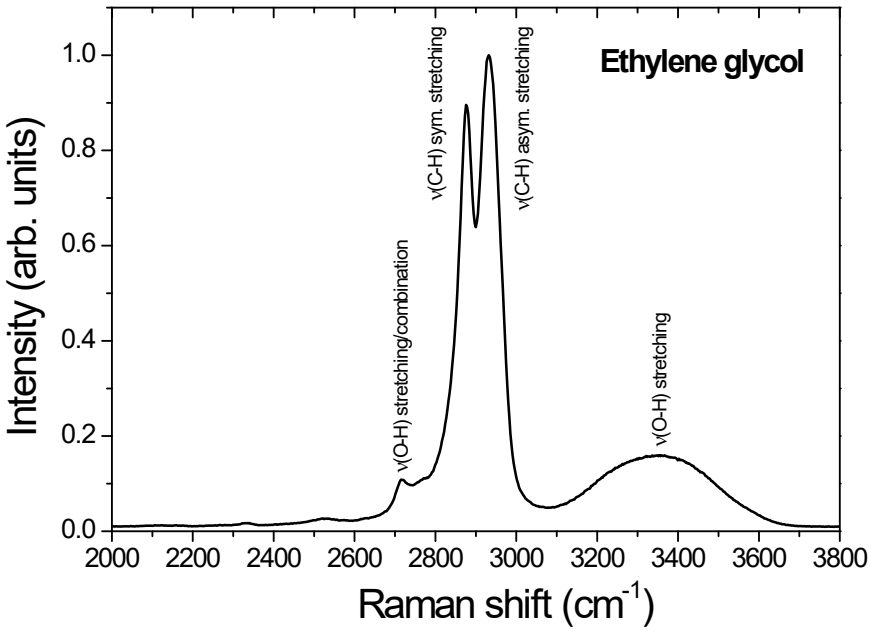

Figure S2B. Room temperature Raman spectrum of EG in the spectral range 2000 – 3800 cm^{-1} with the peaks assigned according to the References in Table S1 & S2.

Table S1. The experimental IR and Raman bands (expressed in cm^{-1} units) of liquid ethylene glycol at room temperature, determined in this work. The assignments and references reporting them previously as well as the corresponding comments are also presented.

IR	Assignment	References	Raman	Assignment	References
Not observed	Not active		347	C-C-O bending	1, 3, 4, 5, 6
Not observed	Not active		481	C-C-O bending (trans)	1, 2, 3, 5, 6, 7
515	C-C-O bending (gauche)	1, 2, 4, 5, 6	523	C-C-O bending (gauche)	1, 2, 3, 4, 5, 6, 7
611 (broad)	O-H torsion	4, 5, 6, 11	Not observed	Not active	
860	C-C stretching	1, 2, 3, 4, 5, 6, 11	860	C-C stretching	1, 2, 3, 4, 5, 6
	CH_2 rocking	8			
881	C-C stretching	11	Not observed	Not active	
	CH_2 rocking	1, 4, 5, 6, 8			
1033	C-O stretching (gauche)	1, 2, 3, 4, 5, 6, 11	1047	C-O stretching (gauche)	1, 2, 3, 4, 5, 6
Not observed	Not active		1066	C-O stretching (trans)	1, 2, 3, 4, 5
				CH_2 rocking	6
1083	C-O stretching	1, 3, 6, 11	1090	C-O stretching	1, 6
	CH_2 rocking	2, 4, 5		CH_2 rocking	2, 3, 4, 5
1204	CH_2 twisting	1, 2, 3, 4, 5, 6, 11	1212	CH_2 twisting	1, 2, 3, 4, 5, 6
1257	CH_2 wagging	1, 3, 11	1268	CH_2 wagging	1
	CH_2 twisting	2, 4, 5, 6, 11		CH_2 twisting	2, 3, 4, 5, 6
1332	CH_2 wagging	1, 4, 5, 6, 11	1284	CH_2 wagging	1, 4, 5, 6
1367	CH_2 wagging	1, 4, 5, 6, 11	Not observed	Not active	
1412	C-O-H bending	1, 3, 4, 5, 6, 11	Not observed	Not active	
1456	CH_2 scissoring	1, 2, 3, 4, 5, 6, 11	1459	CH_2 scissoring	1, 2, 3, 4, 5, 6
Not observed	Not active		2722	O-H stretching	1
				combination	3, 5
2873	C-H symmetric stretching	1, 2, 3, 4, 5, 6, 9, 10, 11	2880	C-H symmetric stretching	1, 2, 3, 4, 5, 6, 9, 10
2937	C-H asymmetric stretching	1, 2, 3, 4, 5, 6, 9, 10, 11	2936	C-H asymmetric stretching	1, 2, 3, 4, 5, 6, 9, 10
3298	O-H stretching	1, 2, 3, 4, 5, 6, 9, 11	3346	O-H stretching	1, 2, 3, 4, 5, 6, 9

Comments on the spectral assignments: It was found that the spectral assignments for the room temperature Raman and IR spectra agreed with the literature within ± 10 cm^{-1}.

Table S2: The experimental Raman bands of crystalline and glassy ethylene glycol, determined in this work. The assignments of the crystalline bands are presented along with the list of references.

Raman, crystal (−150 °C) (cm^{-1})	Assignment	References	Comments	Raman, glass (−150 °C) (cm^{-1})	Assignment	References
41	"wing"	1		45 (broad)	Boson	
75	"wing"	1		Not observed	Not active	
97	"wing"	1		Not observed	Not active	
101	"wing"	1		Not observed	Not active	
117	"wing"	1		115 (shoulder)	Boson	
132	"wing"	1		Not observed	Not active	
148	"wing"	1		Not observed	Not active	
	"external mode"	3				
206	"wing"	1		Not observed	Not active	
	"external mode"	3				
268	"wing"	1		Not observed	Not active	
	"external mode"	3				
319	"wing"	1		Not observed	Not active	
325	C-C-O torsion	3		Not observed	Not active	
355	C-C-O bending	1, 3	Appears at 382 in reference 3	351	C-C-O bending	1, 3, 4, 5, 6
Not observed	Not active			484	C-C-O bending (trans)	1, 2, 3, 5, 6, 7
521	C-C-O bending (gauche)	1, 3	579 and 592 in reference 3	525	C-C-O bending (gauche)	1, 2, 3, 4, 5, 6, 7
526						
657	O-H torsion	3	One peak at 709 in reference 3	Not observed	Not active	
755	O-H torsion	3		Not observed	Not active	
Not observed	Not active			867	C-C stretching	1, 2, 3, 4, 5, 6
1034	No assignment			Not observed	Not active	
1040	C-O stretching (gauche)	1, 3		1047	C-O stretching (gauche)	1, 2, 3, 4, 5, 6
1050						
1057						
Not observed	Not active			1068	C-O stretching (trans)	1, 2, 3, 4, 5
					CH_2 rocking	6
1079	No assignment			Not observed	Not active	
1084	No assignment			Not observed	Not active	
1090	C-O stretching	1, 3	1058 in reference 3	1091	C-O stretching	1, 6
					CH_2 rocking	2, 3, 4, 5
1207	CH_2 twisting	1, 3	1217 in reference 1	1218	CH_2 twisting	1, 2, 3, 4, 5, 6
1234	CH_2 twisting	1, 3	1241 in reference 3	Not observed	Not active	
1269	CH_2 wagging	1	1273 in reference 3	1271	CH_2 wagging	1

	CH_2 twisting	3			CH_2 twisting	2, 3, 4, 5, 6
Not observed	Not active			1293	CH_2 wagging	1, 4, 5, 6
1370	CH_2 wagging	1		Not observed	Not active	
1409	C-O-H bending	1, 3	1382 in reference 1	Not observed	Not active	
1435	No assignment			Not observed	Not active	
1448	No assignment			Not observed	Not active	
1460	CH_2 scissoring	1, 3	1526 in reference 3	1451	CH_2 scissoring	1, 2, 3, 4, 5, 6
2721	O-H stretching	1		2715 as well as 2747	O-H stretching	1
	combination	3			combination	3, 5
2876	C-H symmetric stretching	1, 3	2990 in reference 3	2872	C-H symmetric stretching	1, 2, 3, 4, 5, 6, 9, 10
2932	C-H asymmetric stretching	1, 3	3035 and 3057 in reference 3	2926	C-H asymmetric stretching	1, 2, 3, 4, 5, 6, 9, 10
2954						
3087	O-H stretching	1, 3	3156, 3227, and 3275 in reference 3	3190	O-H stretching	1, 2, 3, 4, 5, 6, 9
3169						
3275						

Comments: The O-H torsional mode in the spectrum of the crystal is reported as a single peak at 709 cm^{-1} in Reference 3, yet two peaks are observed in this work. The 2 peaks assigned to the C-C-O bending mode of the gauche conformer in the crystalline phase are shifted to wavenumbers which are 50-60 cm^{-1} higher in Reference 3. On the other hand, a shift of the C-O stretching mode at 1090 cm^{-1} to lower wavenumbers (1058 cm^{-1}) was observed in Reference 3. The assignments for the Raman spectrum of the crystalline state were found to deviate from the data published previously by as much as 60 cm^{-1}; the C-H and O-H stretching modes deviated by almost 100 cm^{-1}. In addition, five new Raman bands were reported for the crystalline phase; these can likely be attributed to the C-O stretching and the CH_2 scissoring modes.

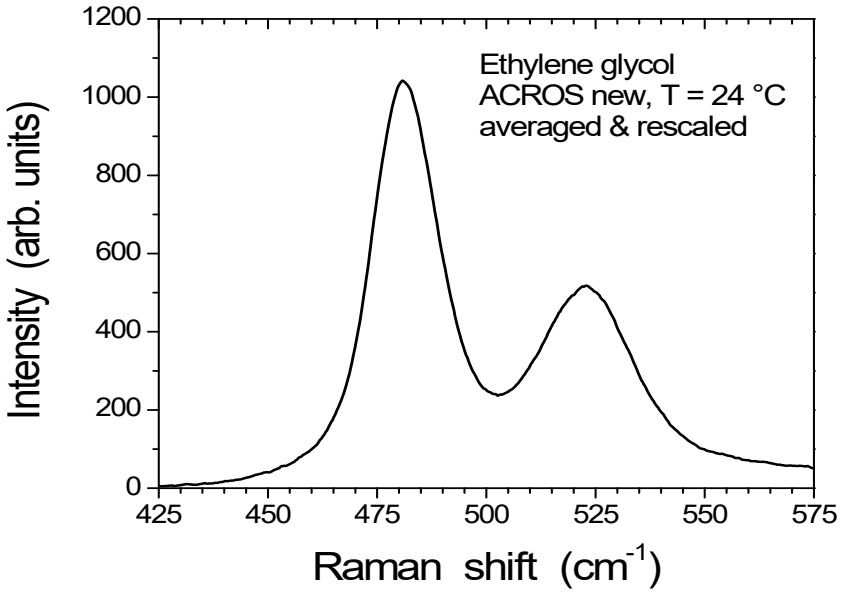

Figure S3. EG Raman spectrum of C-O stretching mode (0.7 cm^{-1} resolution) at +24 °C. The larger band corresponds to the trans conformer while the smaller peak corresponds the gauche conformer.

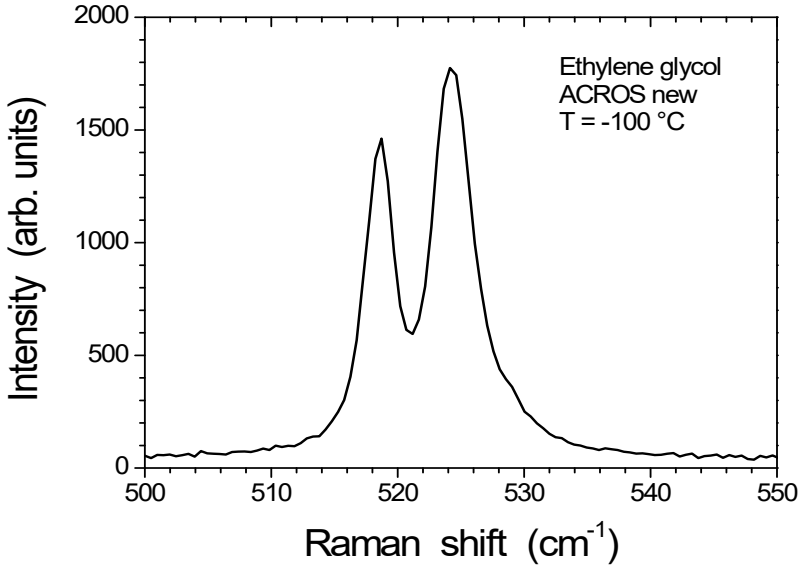

Figure S4. EG Raman spectrum of the gauche band in the C-O stretching mode (0.7 cm^{-1} resolution) at −100 °C. The band splits into two peaks in the crystalline EG spectrum, while the peak corresponding to the trans conformer is not observed.

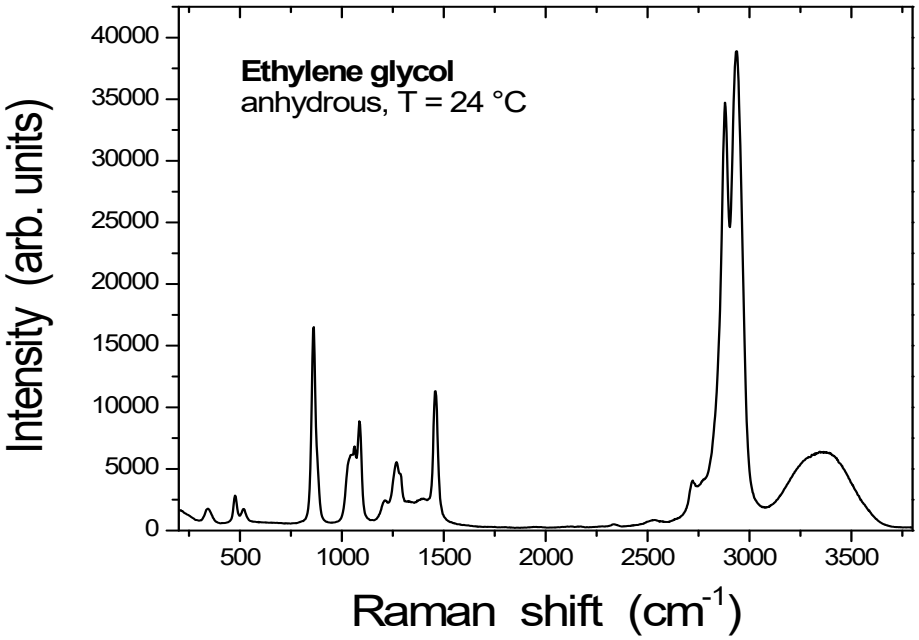

Figure S5. The room temperature Raman spectrum of EG (~9 cm^{-1} resolution).

The Clausius–Mossotti relation [12] was employed to calculate the high frequency single-molecule mean polarizability (α) of EG in the temperature range from −70 to +15 °C:

$$\frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2} = \frac{4\pi}{3} \times N \times \alpha \tag{S1}$$

Where ε_∞ is the dielectric constant at the high frequency limit and N is the number density of the EG molecules. The dielectric constants needed were taken from reference 34 (in the main text) and our extrapolated measured densities were utilized [Reference 16 in the main text].

An increase in polarizability of about one order of magnitude occurs in this interval.

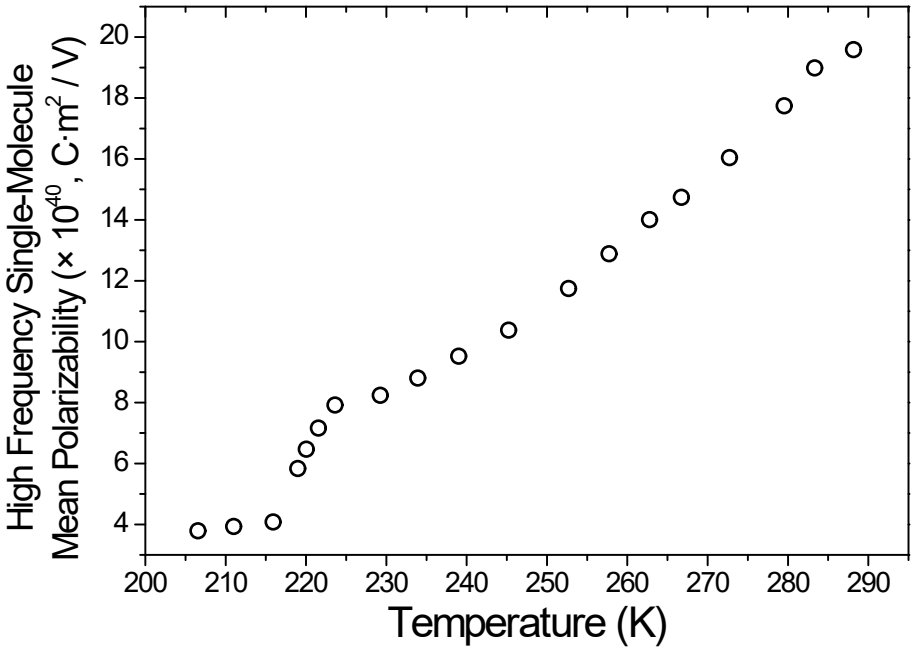

Figure S6. The high frequency single-molecule mean polarizability of EG in the temperature range from −70 to +15 °C.

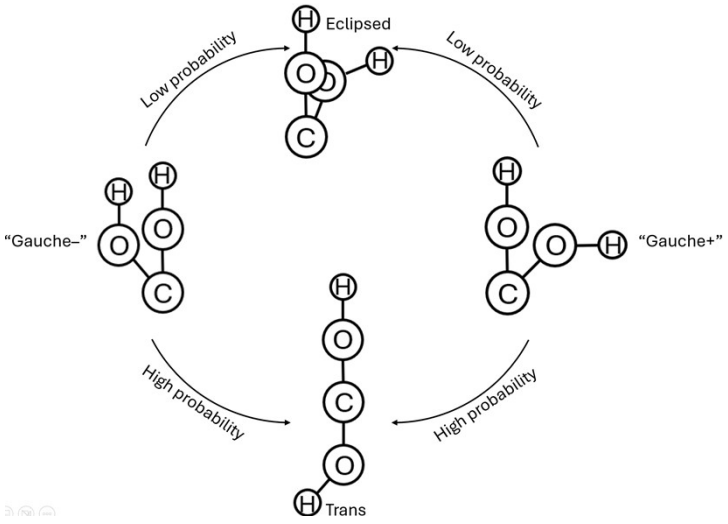

Figure S7. Reaction paths of G → T enantiomer transformation according to the data from Reference 43 in the main text. The difference in reaction probabilities is due to the difference in activation energies (ΔE = 15.3 kJ/mol)

References

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