

Supporting Information

Do Material Discontinuities in Silica Affect Vibration Modes?

*Victor V. Volkov, David J. Belton, Carole C. Perry**

Interdisciplinary Biomedical Research Centre, School of Science and Technology, Nottingham Trent University, Clifton Lane, Nottingham NG11 8NS, United Kingdom.

The main results of our theoretical studies were obtained using Density Functional Theory with the 6-31G(d) basis set and the restricted B3LYP functional within the Gaussian 09 program package.

The basis set the 6-31G(d) basis set is the smallest we can use to receive sensible results on the time scale of several months. However, since we work with Si atoms, the level of the theory is marginal because the gap between the 3p and 2d orbitals is small enough that the d functions from the 6-31G(d) basis set is really a valence basis set so there are no polarization functions in the basis. Without that DFT correlation does not behave nearly as well as it should.

It is clear that the selected basis should not allow us to obtain frequencies and atomic displacements of the normal modes at high quality. Nevertheless, it allows us to anticipate well the main trends.

However, to confirm that our estimated electronic properties would not suffer due to the level of theory we also conducted single point population analysis using 6-31G(2d,p) basis set. The basis set 6-31G(2d,p) is the very next level suitable for effective modelling of the considered structures. Accordingly, In Figures S1, S2 and S3 we compare HOMO and LUMO, electrostatic potentials and Total Densities of States for the structures using the two basis sets, respectively.

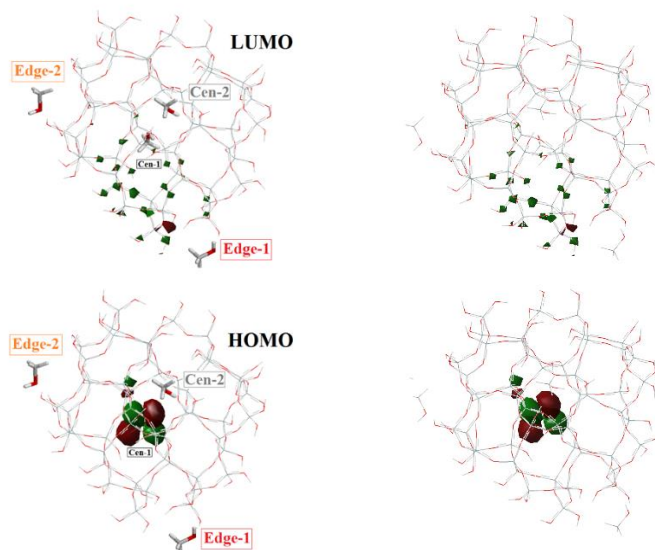


Figure S1. Left side: HOMO and LUMO anticipated using 6-31G(d) basis set. Right side: HOMO and LUMO anticipated using 6-31G(2d,p) basis set.

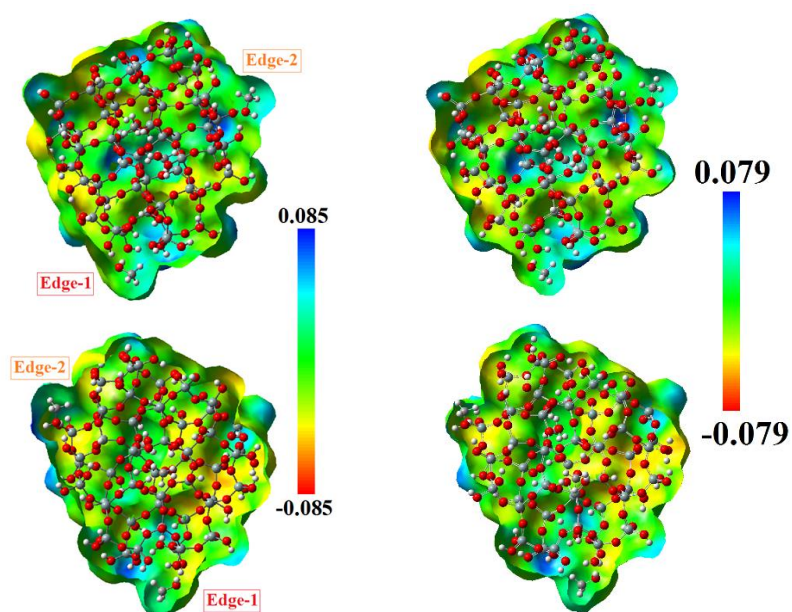


Figure S2. Left side: Electrostatic Potential mapped onto electron density anticipated using 6-31G(d) basis set: two images represent views from the opposite sides of the cluster. Right side: Electrostatic Potential mapped onto electron density anticipated using 6-31G(2d,p) basis set: two images represent views from the opposite sides of the cluster.

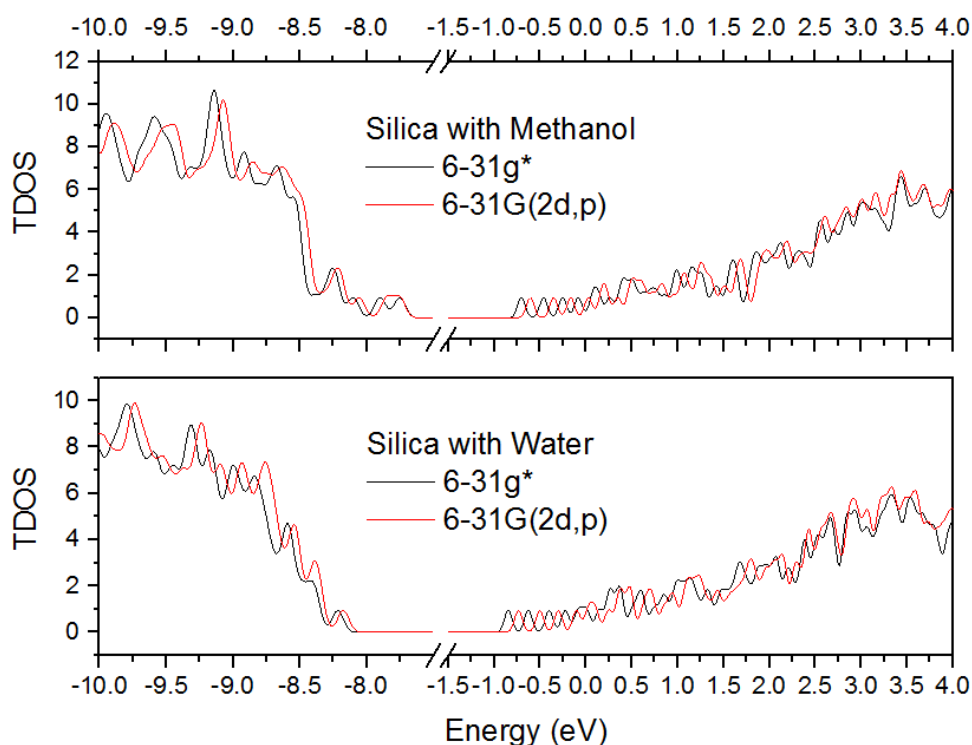


Figure S3. Total Densities of States for the considered silica cluster with methanol molecules and with water molecules if placed in the positions of the methanols.

The results in figures S1, S2 and S3 indicate that there is very little difference in electronic properties when we use a different basis set. These results suggest that with the used basis we can discuss the main trends in the engineered systems.

To assign IR absorption at 2140 cm^{-1} , we conducted DFT anharmonic analysis for a methanol cluster built of four $\text{CD}_3\text{-OH}$ molecules. Accordingly, in Figure S4, we compare FTIR spectrum of $\text{CD}_3\text{-OH}$ added as impurity in H_2O with calculated Infrared absorption intensities of fundamental normal modes, combinations and overtones in the spectral region characteristic to C-D stretching vibrations.

Theory anticipates that in the spectral region from 2120 to 2200 cm^{-1} methanol molecules may show relatively weak Infrared absorption due to combinations of C-O stretchings (at about 1013 cm^{-1}) and normal modes where symmetric C-D umbrella bending of the methyl group is mixed with C-O stretching (at about 1164 cm^{-1}). Also, at the blue side of this spectral region,

we may expect contributions of overtones of D-C-D bending, the fundamentals of which are at about 1110 cm^{-1} .

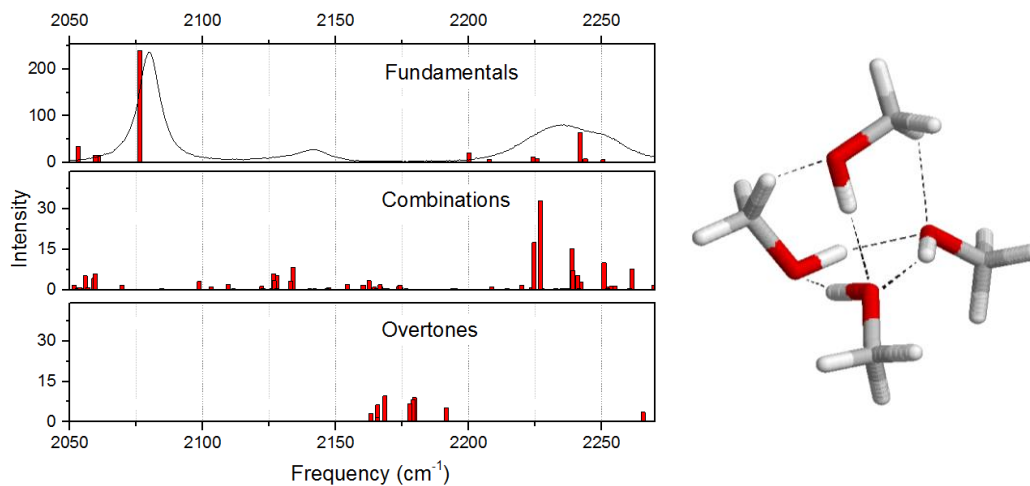


Figure S4. Red bars: intensities of Infrared active fundamental modes, combinations and overtones using DFT anharmonic normal mode analysis for a methanol cluster built of four CD₃-OH molecules in the spectral region specific to C-D vibrations. Black line: FTIR spectrum of CD₃-OH impurity in H₂O as reported in Figure 1 in the main text.