Assessing the Predictability of anharmonic Vibrational Modes at the Example of Hydroxyl Groups – Adhoc Construction of localised Modes and the influence of structural Solute-Solvent Motifs – Supplementary Material

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Table S1: Angle between the normal coordinate $q$ and the mode constructed by a weighted movement of hydrogen and oxygen $\bar{q}$ in degrees and respective difference of the reduced mass $\Delta \mu = \mu_n - \mu_c$ in mg/mol.

|          | $\cos\langle q | \bar{q} \rangle$ in degrees | $\Delta \mu$ in mg/mol |
|----------|----------------------------------------|------------------------|
| Vacuum   | SMD (CCl$_4$)                          |                        |
| Methanol | 1.12                                   | 1.16                   |
| Phenol   | 0.96                                   | 0.91                   |
| Thymol   | 0.93                                   | 0.88                   |

\[
A = \frac{1}{\|\Delta q\|^2} \begin{pmatrix} 1 & \cdots & 1 \\ \cdots & \cdots & \cdots \\ 1 & \cdots & 1 \\ \cdots & \cdots & \cdots \\ 1 & -2 & 1 \\ -2 & 1 & 1 \end{pmatrix}, \quad B = \frac{1}{12} \begin{pmatrix} 10 & 1 \\ 1 & 10 & 1 \\ \cdots & \cdots & \cdots \\ 1 & -2 & 1 \\ -2 & 1 & 1 \end{pmatrix}
\]

(S1)
Figure S1: Energy difference between Numerov calculations and the corresponding analytical solution of the Morse potential \((D = 366.48 \text{kJ/mol}, \alpha = 2.511 \text{Å}^{-1})\) as a function of the grid density for different stencil sizes and selected energy eigenvalues \(E_n (n = 0, 1, 5, 10)\).

Figure S2: Energy difference between Numerov calculations and the corresponding analytical solution of the Morse potential \((D = 732.96 \text{kJ/mol}, \alpha = 1.776 \text{Å}^{-1})\) as a function of the grid density for different stencil sizes and selected energy eigenvalues \(E_n (n = 0, 1, 5, 10)\).
Figure S3: Comparison of the OH potential energy scans at BP86 and B3LYP/6-311++G(3df,3pd) in vacuum solvation resulting from the variation of the OH distance (top) as well as potential energy scans along the analytical (middle) and constructed (bottom) normal coordinate of the OH vibrational mode. The plots for phenol and thymole are depicted with constant energy cutoffs of 100 and 200 kJ/mol, respectively.
Figure S4: Comparison of the 3-point (green), threshold fit 10kJ/mol (blue) and “best” (red) Morse fits to the potential energy scan along the analytical normal coordinate of the thymol OH vibrational mode at B3LYP/6-311++G(3df,3pd) level in implicit solvent. The observed minor differences in the Morse potentials lead to deviations of up to 80 and 160 cm$^{-1}$ in the fundamental and first overtone wave numbers. Moreover, the wrong asymptotic behaviors at large distances is clearly visible, thus large errors in the prediction of overtones beyond the first can be expected.