ELECTRONIC SUPPLEMENT FOR:

The benefits of alternation and alkylation: Large amplitude hydrogen bond librational modes of alcohol trimers and tetramers

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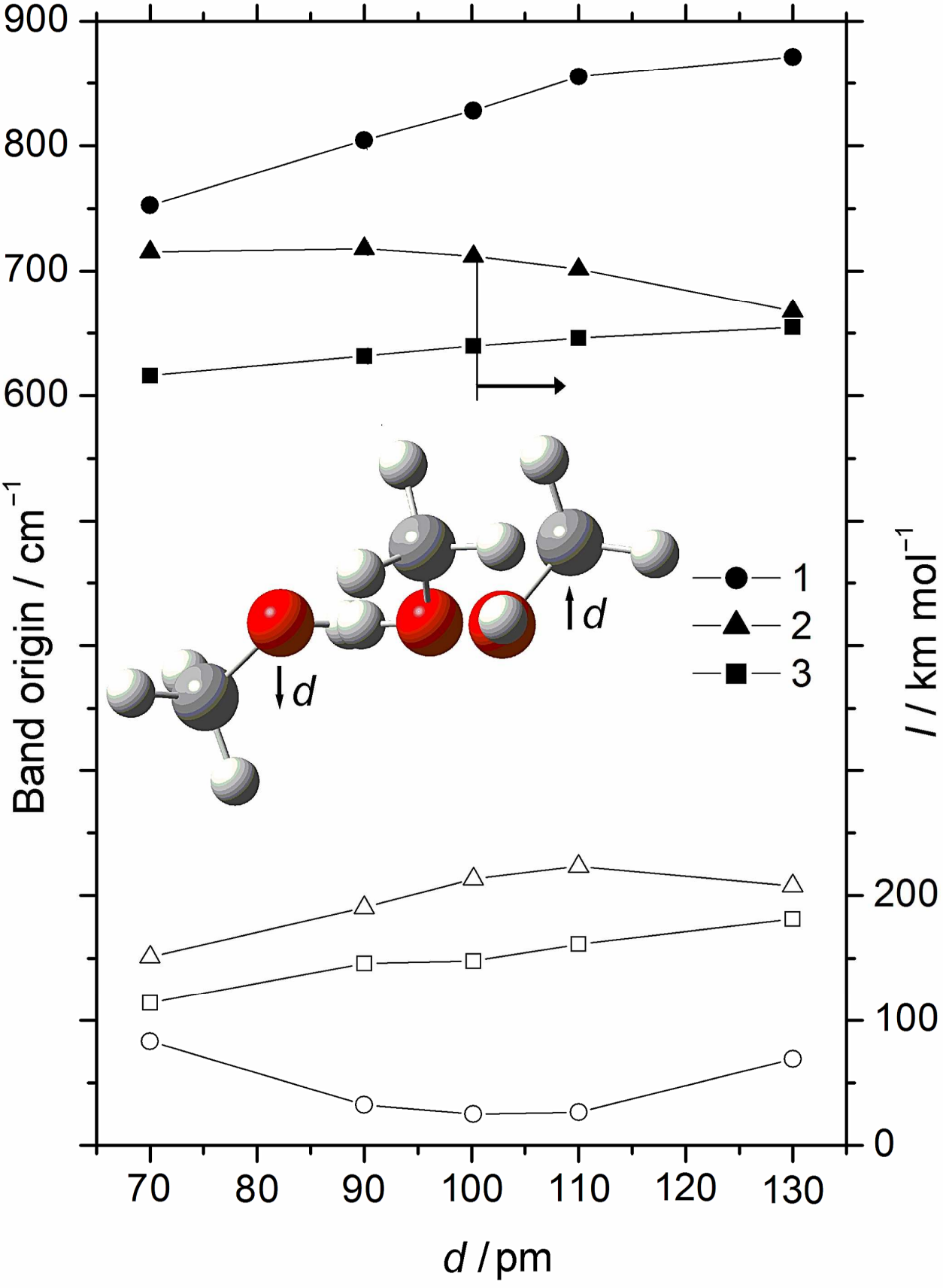
As shown in Figs. S1 and S2, the evolution of the splitting and intensity patterns from methanol trimer to *t*-butyl trimer is inconclusive for two B3LYP/6-311++G(3df,2p) distortion paths of the alkyl groups away from the hydrogen bond plane, partly due to the lack of symmetry. The splitting pattern indicates an increased puckering of the more bulky groups, whereas the intensity pattern is very sensitive to the chosen path and gives contradictory results.


900
800
700
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Band origin / cm^{-1}
200
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I / km mol^{-1}
70
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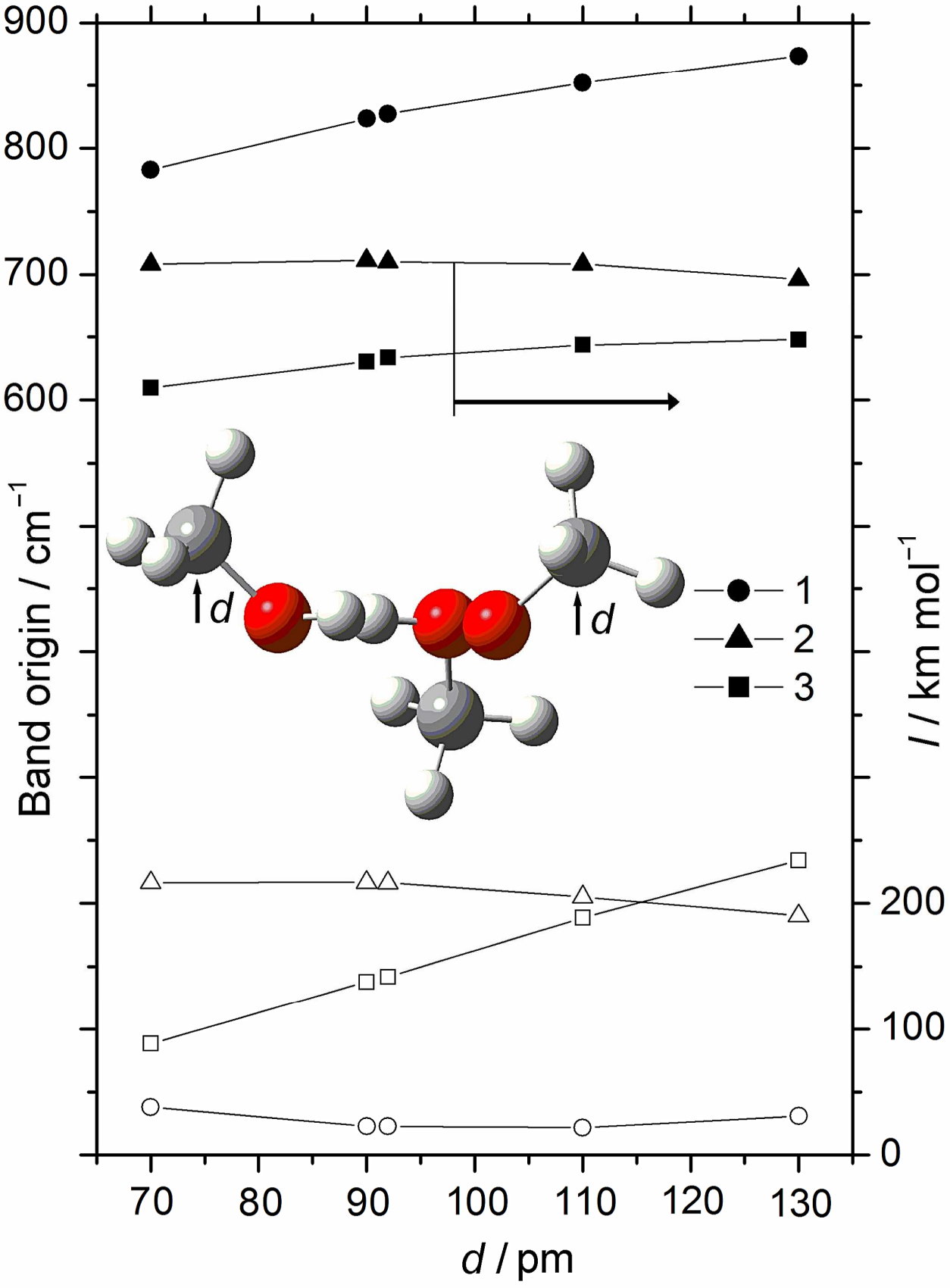
110
120
130
d / pm
1
2
3
d
d

Figure S1: Predicted harmonic band origins and corresponding IR band strengths of the methanol trimer at different restrained B3LYP/6-311++G(3df,2p) optimized geometries, fixing one methyl carbon at a distance d above the oxygen plane and the other one at the same distance below the oxygen plane. The vertical line indicates the position (d=105 pm) where the experimental wavenumber ratio matches the predicted one for the two IR-intense bands (squares and triangles). It is reasonably close to the fully optimized value d=100 pm (d=93 pm for the third methyl carbon), but the observed intensity ratio is not reproduced, thus weakening the analysis. The arrow indicates how the experimental wavenumber ratio for t-butyl alcohol trimer is predicted to translate into a change in d.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Band origin / cm^{-1}
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d
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I / km mol^{-1}
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120
130
d / pm

Figure S2: Predicted harmonic band origins and corresponding IR band strengths of the methanol trimer at different restrained B3LYP/6-311++G(3df,2p) optimized geometries, fixing two methyl carbons at a distance d above the oxygen plane without constraints on the third one. The vertical line indicates the position (d=98 pm) where the experimental wavenumber ratio matches the predicted one for the two IR-intense bands (squares and triangles). It is reasonably close to the fully optimized value d=92 pm (d=−108 pm for the third methyl carbon), but the observed intensity ratio cannot be reproduced in a meaningful range of d, thus weakening the analysis. The arrow indicates how the experimental wavenumber ratio for *t*-butyl alcohol trimer is predicted to translate into a change in d, namely increasing with increasing bulkiness. The observed decrease in relative intensity of the lowest frequency peak indicates a decrease in d with increasing bulkiness, at variance with the frequency splitting trend.