Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

# Electronic Supplementary Information:

# Bracketing Subtle Conformational Energy Differences Between Self-Solvated and Stretched Trifluoropropanol

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# 1. Torsional Potential Energy Surface Fit

Given below are the parameters of the Fourier-series fit to the LCCSD(T)/aVTZ potential energy surface:

$$\frac{V(\tau_1, \tau_2)}{\mathrm{kJ \cdot mol^{-1}}} = \sum_{i,j=0}^{7} c_{i,j} \cos(i\tau_1) \cos(j\tau_2) + \sum_{k,l=1}^{7} d_{k,l} \sin(k\tau_1) \sin(l\tau_2)$$

| $i$ | $j$ | $c_{i,j}$ |
|---|---|---|
| 0 | 0 | 13.388942 |
| 0 | 1 | 1.614865 |
| 0 | 2 | 1.592717 |
| 0 | 3 | 2.534797 |
| 1 | 0 | 5.127941 |
| 1 | 1 | −2.320030 |
| 1 | 2 | 0.424313 |
| 1 | 3 | 0.128629 |
| 2 | 0 | 3.591949 |
| 2 | 2 | 0.336128 |
| 2 | 3 | 0.086954 |
| 3 | 0 | 6.430856 |
| 3 | 1 | 0.808463 |
| 3 | 2 | 0.743297 |
| 3 | 3 | 0.357398 |
| 4 | 2 | 0.435199 |
| 4 | 3 | 0.192823 |
| 4 | 4 | 0.110051 |
| 5 | 0 | 0.107473 |
| 5 | 1 | −0.115732 |
| 5 | 3 | 0.089062 |
| 5 | 4 | 0.069675 |
| 6 | 0 | 0.217518 |
| 6 | 2 | −0.117298 |
| 7 | 2 | −0.103599 |

| $k$ | $l$ | $d_{k,l}$ |
|---|---|---|
| 1 | 1 | 2.224015 |
| 1 | 2 | 0.400922 |
| 1 | 3 | −0.231037 |
| 1 | 4 | −0.110873 |
| 2 | 1 | 0.218720 |
| 2 | 2 | −0.239635 |
| 2 | 3 | −0.178576 |
| 2 | 4 | −0.122536 |
| 3 | 1 | −1.764695 |
| 3 | 2 | −0.533636 |
| 3 | 3 | −0.322108 |
| 3 | 4 | −0.120435 |
| 4 | 1 | −0.136208 |
| 4 | 2 | −0.434288 |
| 4 | 3 | −0.182891 |
| 4 | 4 | −0.117750 |
| 5 | 3 | −0.082123 |
| 5 | 4 | −0.078526 |
| 6 | 2 | 0.083342 |
| 7 | 1 | −0.067688 |

## 2. Band Intensity and Conformer Population Ratios

Given below are the observed band intensity ratios *F* of the TFP (Tt/Gg′) and EtOH (g/t) measurements, together with deduced conformer ratios *S* using calculated intensity ratios *C* (averages of MP2 and B3LYP calculations). Errors of last digits are given in parentheses.

| | *C* | $\vartheta_n$ / °C | *F* | *S* |
|---|---|---|---|---|
| C1–C2 | 0.723(4) | 25 | 0.21(2) | 0.29(3) |
| | | 80 | 0.22(2) | 0.30(2) |
| | | 150 | 0.25(3) | 0.34(4) |
| C1–H | 1.06(2) | 25 | 0.19(2) | 0.18(2) |
| | | 80 | 0.21(1) | 0.20(2) |
| | | 150 | 0.23(2) | 0.22(2) |
| O–H | 2.16(3) | 25 | 0.50(7) | 0.23(2) |
| | | 80 | 0.52(7) | 0.24(6) |
| | | 150 | 0.66(7) | 0.31(6) |
| | | | | |
| EtOH O–H | 1/1.5(1) [1] | | | |
| 1 mm | | 33 | 0.72(2) | 1.08(11) |
| | | 80 | 0.78(3) | 1.17(13) |
| | | 150 | 0.84(3) | 1.26(13) |
| 3 mm | | 33 | 0.56(2) | 0.83(9) |
| | | 80 | 0.59(1) | 0.89(8) |
| | | 150 | 0.64(1) | 0.96(8) |
| 6 mm | | 33 | 0.40(7) | 0.60(15) |
| | | 80 | 0.44(6) | 0.66(14) |
| | | 150 | 0.54(9) | 0.81(18) |

[1] T. Wassermann and M. A. Suhm. Ethanol Monomers and Dimers Revisited: A Raman Study of Conformational Preferences. *J. Phys. Chem. A*, 114 (2010), 8223-8233.

# 3. Frequency Calculations and Vibrational Assignments

Given below are harmonic wavenumbers $\omega$ (in cm$^{-1}$) and $\sigma'$ values (in $10^{-35}$ m$^2$sr$^{-1}$) from B3LYP/aVTZ, MP2/aVTZ and LMP2/aVTZ calculations for the Gg′ and Tt conformers. Also given are proposed assignments to experimentally observed bands $\tilde{\nu}$ ("br" = broad). The wavenumbers of the C2–C3, symmetric C1–H and O–H stretching bands that were fixed to experimental values in the corresponding plots are printed in red (see the main text). The wavenumbers of the common Gg′/Tt bands that were used for the experimental "harm+obs" ZPVE update are underlined.

## Gg′

| B3LYP/aVTZ | | MP2/aVTZ | | LMP2/aVTZ | | |
|---|---|---|---|---|---|---|
| $\omega$ | $\sigma'$ | $\omega$ | $\sigma'$ | $\omega$ | $\tilde{\nu}$ | Assignment |
| 56 | 2.47 | 59 | 2.14 | 59 | | |
| 138 | 0.24 | 155 | 0.20 | 151 | | |
| 215 | 0.73 | 221 | 0.61 | 220 | 220 | |
| 308 | 2.12 | 312 | 1.80 | 312 | 311 | |
| 339 | 1.51 | 355 | 1.05 | 345 | 310 | $\tau_2$ (br) |
| 376 | 1.59 | 384 | 1.45 | 382 | 379 | |
| 473 | 0.86 | 478 | 0.81 | 478 | 478 | |
| 529 | 0.49 | 537 | 0.48 | 537 | | |
| 545 | 2.16 | 556 | 1.89 | 554 | 553 | $CF_3$ deform |
| 623 | 0.83 | 634 | 0.71 | 633 | 631 | $CF_3$ deform (br) |
| 789 | 7.45 | 808 | 7.44 | 805 | 797 | C2–C3 stretch |
| 875 | 1.90 | 889 | 1.86 | 886 | 872 | |
| 943 | 1.48 | 958 | 1.19 | 956 | 945 | (br) |
| 1004 | 2.11 | 1029 | 2.41 | 1026 | | |
| 1070 | 0.88 | 1105 | 0.97 | 1100 | 1072 | C1–C2 stretch (br) |
| 1116 | 0.79 | 1147 | 1.00 | 1146 | | |
| 1140 | 2.01 | 1166 | 1.65 | 1162 | | |
| 1225 | 0.73 | 1248 | 0.77 | 1245 | 1226 | (br) |
| 1258 | 0.40 | 1286 | 0.29 | 1283 | | |
| 1291 | 0.92 | 1308 | 0.81 | 1307 | 1284 | (br) |
| 1387 | 1.36 | 1397 | 1.38 | 1396 | 1359 | |
| 1394 | 0.86 | 1416 | 0.76 | 1414 | 1383 | |
| 1426 | 0.73 | 1434 | 0.71 | 1434 | 1402 | |
| 1468 | 1.14 | 1482 | 0.93 | 1480 | 1446 | (br) |
| 1510 | 1.91 | 1529 | 1.65 | 1526 | 1479 | C1–H scissor (br) |
| 3014 | 16.48 | 3073 | 15.53 | 3073 | 2904 | symm. C1–H stretch |
| 3059 | 13.39 | 3109 | 12.92 | 3105 | | |
| 3092 | 14.06 | 3157 | 10.55 | 3157 | | |
| 3108 | 5.68 | 3175 | 4.86 | 3173 | | |
| 3815 | 5.01 | 3840 | 4.53 | 3841 | 3668 | OH stretch |
| $\sum\omega$=37585 cm$^{-1}$ | | 38246 cm$^{-1}$ | | 38186 cm$^{-1}$ | | |

# Tt

| B3LYP/aVTZ | | MP2/aVTZ | | LMP2/aVTZ | | |
|---|---|---|---|---|---|---|
| $\omega$ | $\sigma'$ | $\omega$ | $\sigma'$ | $\omega$ | $\tilde{\nu}$ | Assignment |
| 75 | 1.65 | 77 | 1.45 | 78 | | |
| 95 | 1.88 | 105 | 1.64 | 106 | | |
| 169 | 0.75 | 171 | 0.68 | 171 | | |
| 259 | 3.57 | 259 | 2.93 | 263 | 216 | $\tau_2$ (br) |
| 348 | 3.39 | 354 | 2.82 | 352 | 356 | |
| 359 | 0.41 | 366 | 0.35 | 365 | | |
| 392 | 1.23 | 397 | 1.27 | 397 | 396 | |
| 533 | 0.63 | 540 | 0.62 | 540 | | |
| 548 | 1.48 | 557 | 1.39 | 556 | 550 | $CF_3$ deform |
| 661 | 1.71 | 671 | 1.66 | 669 | 668 | $CF_3$ deform |
| 805 | 0.21 | 814 | 0.15 | 814 | | |
| 843 | 5.41 | 863 | 5.36 | 859 | 848 | C2–C3 stretch |
| 1003 | 1.30 | 1028 | 1.21 | 1026 | | |
| 1024 | 2.61 | 1053 | 3.35 | 1049 | 1031 | C1–C2 stretch |
| 1046 | 2.60 | 1074 | 2.66 | 1068 | 1048 | |
| 1140 | 2.08 | 1178 | 1.60 | 1175 | | |
| 1172 | 0.18 | 1191 | 0.15 | 1189 | | |
| 1250 | 0.88 | 1260 | 0.88 | 1259 | | |
| 1256 | 0.33 | 1275 | 0.46 | 1273 | | |
| 1257 | 0.21 | 1283 | 0.19 | 1280 | | |
| 1328 | 2.16 | 1344 | 1.85 | 1341 | 1310 | (br) |
| 1377 | 0.19 | 1401 | 0.28 | 1398 | | |
| 1461 | 0.04 | 1473 | 0.13 | 1471 | | |
| 1483 | 1.94 | 1498 | 1.63 | 1494 | | |
| 1532 | 1.33 | 1550 | 1.18 | 1546 | 1557 | C1–H scissor (br) |
| 3007 | 17.90 | 3066 | 16.29 | 3065 | 2919 | C1–H symm. stretch |
| 3040 | 9.98 | 3118 | 7.97 | 3116 | | |
| 3068 | 12.96 | 3119 | 11.54 | 3118 | | |
| 3115 | 4.17 | 3184 | 3.52 | 3182 | | |
| 3827 | 10.98 | 3846 | 9.71 | 3844 | 3682 | OH stretch |
| $\sum\omega$=37474 cm$^{-1}$ | | 38116 cm$^{-1}$ | | 38065 cm$^{-1}$ | | |

# 4. Low-Frequency Spectral Region

Shown below are jet spectra in the low-frequency and fingerprint regions and comparisons with unscaled harmonic B3LYP/aVTZ and LMP2/aVTZ calculations, the latter using the spectral intensities from the former. All calculations assume a relative Tt:Gg′ ratio of 0.2. Proposed band assignments that have been used in the experimental ZPVE update are indicated by dashed lines. In the 1200–1600 cm$^{-1}$ region, assignments were made based on the depolarization ratios $\delta$ (annotated) which govern the intensity of the Q branches, with the latter vanishing for depolarized bands ($\delta = 6/7 \approx 0.86$).

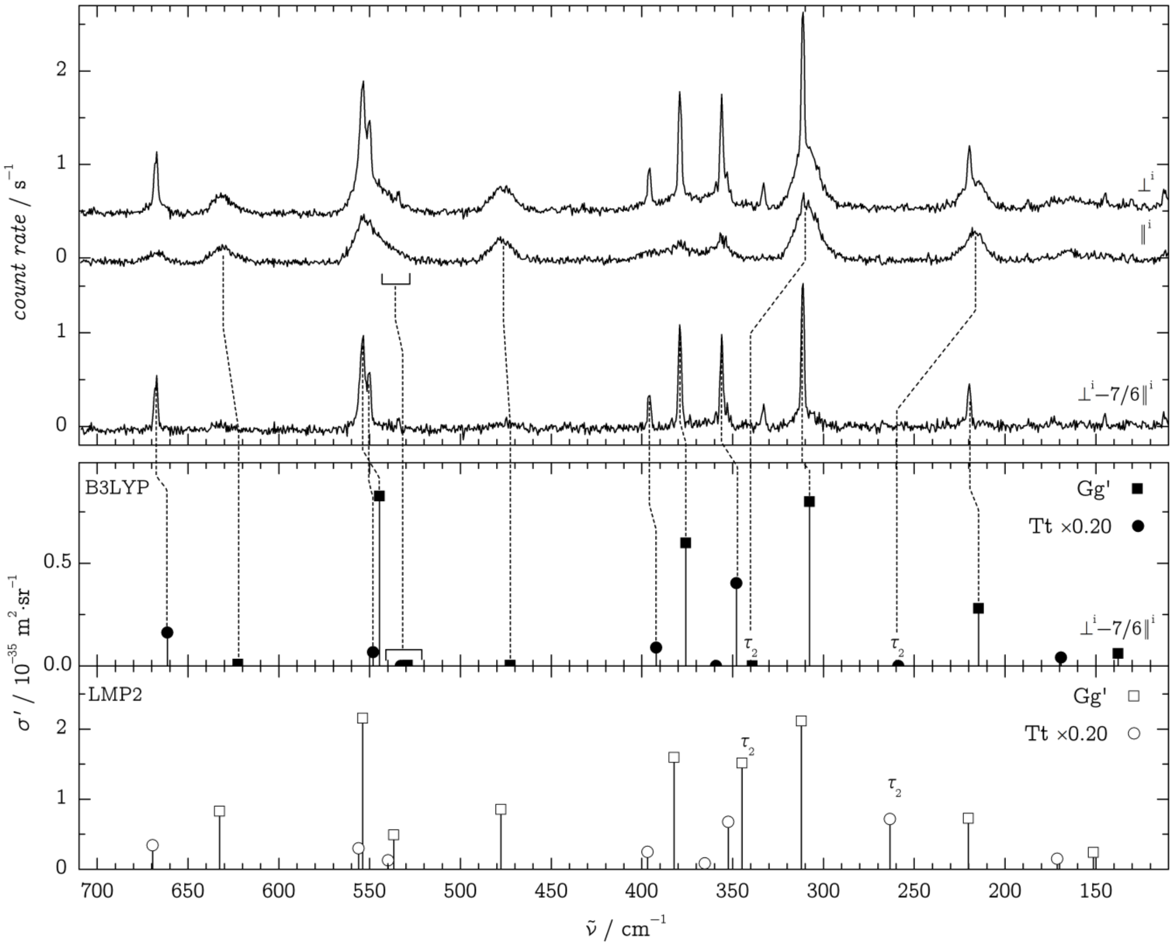

Figure S 1: Polarization-affected Raman jet spectra and comparison with calculations in the 110–710 cm$^{-1}$ region. The LMP2 predictions are combined with unpolarized B3LYP intensities (because LMP2 intensities were unavailable and to illustrate the close match between LMP2 and scaled B3LYP band positions).

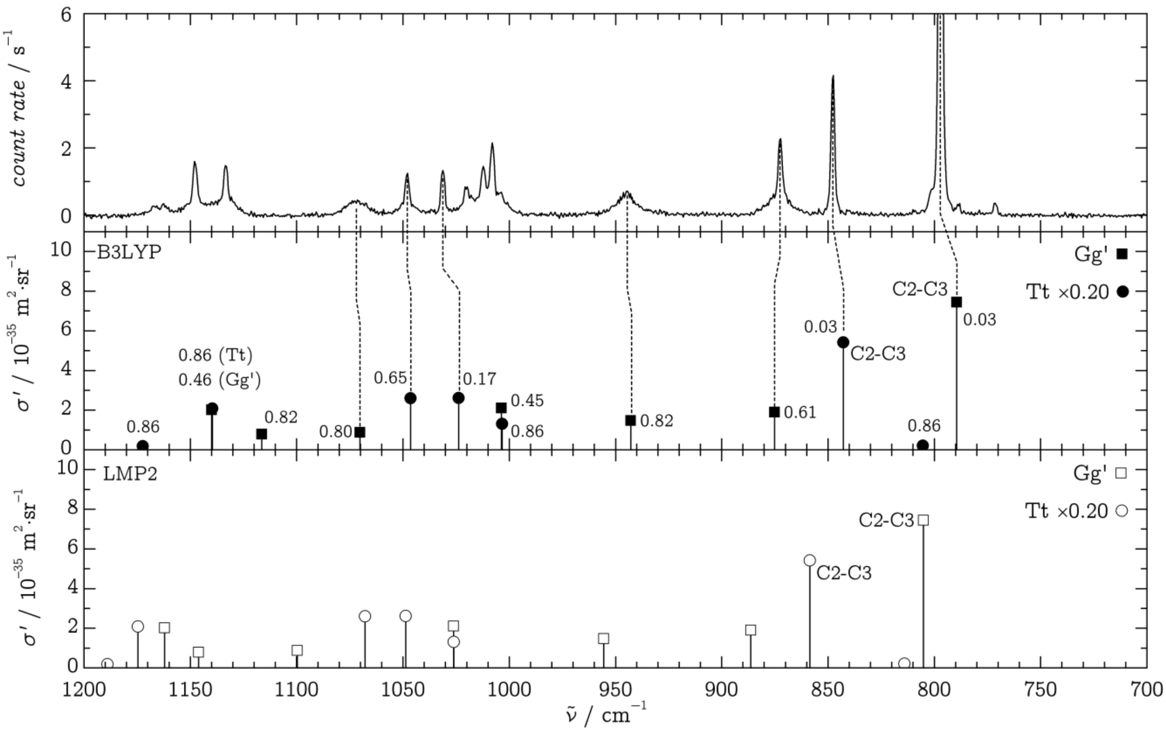

Figure S 2: Raman jet spectrum and harmonic calculations in the 700–1200 cm$^{-1}$ region. Annotated are the depolarization ratios $\delta$ (≤ 6/7), whereby Q branches become less intense for larger $\delta$ and are completely absent at $\delta$ = 6/7 ≈ 0.86. Because LMP2 intensities are unavailable, B3LYP intensities are adopted in the lower trace.

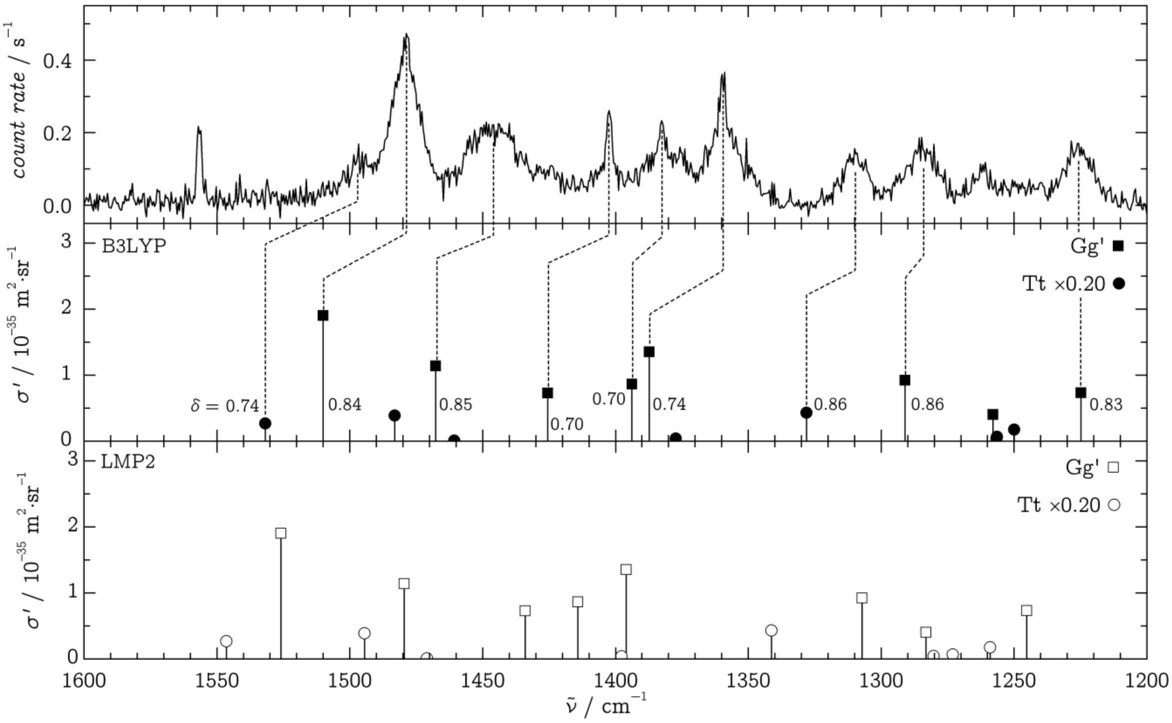

Figure S 3: Raman jet spectrum and harmonic calculations in the 1200–1600 cm$^{-1}$ region. Annotated are the depolarization ratios $\delta$ (≤ 6/7), whereby Q branches become less intense for larger $\delta$ and are completely absent at $\delta$ = 6/7 ≈ 0.86. Because LMP2 intensities are unavailable, B3LYP intensities are adopted in the lower trace.