Supporting Information for:
Quantum Calculations on a New CCSD(T) Machine-Learned Potential Energy Surface
Reveal the Leaky Nature of Gas-Phase Trans and Gauche Ethanol Conformers

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Comparison of energies between different basis sets

Table S1: Single-point energies (cm$^{-1}$) of four stationary points at different level of theory relative to $trans$ minima.

| Geom. | CCSD(T)-F12/aVDZ | CCSD(T)/aVQZ | CCSD(T)/aVQZ$^a$ |
|-------|------------------|--------------|-------------------|
| Gauche | 42               | 45           | 45                |
| TS1   | 389              | 383          | 383               |
| TS2   | 438              | 424          | 423               |

$^a$ From Ref. 1.

Comparison between correction and DFT energies

Figure S1: Plot of $\Delta V_{CC-LL}$ (relative to the reference value i.e. -35 732 cm$^{-1}$) vs DFT energy relative to the CH$_3$CH$_2$OH minimum value with the indicated number of training data sets.
Harmonic frequencies:

Isomerization TSs (Eclipsed and Syn)

Table S2: Comparison of harmonic frequencies (in cm$^{-1}$) between $V_{LL\rightarrow CC}$ PES and the corresponding $ab$ initio (CCSD(T)-F12a/aug-cc-pVDZ) ones of both eclipsed and syn TSs of Ethanol.

| Mode | \(\Delta\)-ML PES | \(ab\) initio | Diff. | \(\Delta\)-ML PES | \(ab\) initio | Diff. |
|------|------------------|---------------|-------|------------------|---------------|-------|
| 1    | 267i             | 287i          | 20i   | 332i             | 300i          | -32i  |
| 2    | 261i             | 256i          | -5    | 270i             | 271i          | 1i    |
| 3    | 420i             | 416i          | -4    | 411i             | 414i          | 3i    |
| 4    | 800i             | 797i          | -3    | 812i             | 807i          | -5    |
| 5    | 899i             | 899i          | 0     | 892i             | 892i          | 0     |
| 6    | 1058i            | 1064i         | 6     | 1057i            | 1061i         | 4     |
| 7    | 1106i            | 1106i         | 0     | 1105i            | 1109i         | 4     |
| 8    | 1133i            | 1132i         | -1    | 1186i            | 1187i         | 1     |
| 9    | 1285i            | 1285i         | 0     | 1307i            | 1298i         | -9    |
| 10   | 1370i            | 1358i         | -12   | 1308i            | 1306i         | -2    |
| 11   | 1399i            | 1397i         | -2    | 1406i            | 1402i         | -4    |
| 12   | 1428i            | 1427i         | -1    | 1446i            | 1440i         | -6    |
| 13   | 1485i            | 1486i         | 1     | 1493i            | 1493i         | 0     |
| 14   | 1500i            | 1508i         | -2    | 1507i            | 1502i         | -5    |
| 15   | 1522i            | 1520i         | -2    | 1534i            | 1539i         | 5     |
| 16   | 3020i            | 3028i         | 8     | 3015i            | 3027i         | 12    |
| 17   | 3028i            | 3034i         | 6     | 3027i            | 3030i         | 3     |
| 18   | 3059i            | 3069i         | 10    | 3054i            | 3061i         | 7     |
| 19   | 3112i            | 3123i         | 1     | 3103i            | 3106i         | 3     |
| 20   | 3123i            | 3124i         | 1     | 3109i            | 3113i         | -6    |
| 21   | 3896i            | 3890i         | -6    | 3872i            | 3865i         | -7    |
Functional form for the 2-D CH$_3$ and OH torsional potential and calculations performed with it.

The functional form of the 2-D fit to the methyl and OH torsional motions shown in the 2-D contour plot of the main text is presented here. The best values of the variables in Table S3 were obtained by simultaneously fitting five cuts of the OH and CH$_3$ torsion calculated from the full-dimensional PES. There were two unknown parameters. These cuts are shown in Figs. 4 and 8 of the main text and in Fig. S2, below. The fits are virtually indistinguishable from the data and produced the values shown in the Table.

$$V_{OH}(\phi) = 0.5 \sum_{n=1}^{4} V_{nOH}(1 - \cos(n\phi)),$$

$$V_{CH3}(\theta) = V_{CH3}^{\phi=0}(0.5)(1 - \cos(3\theta)),$$

$$\text{Correction}(\phi) = 1 + \left( \sum_{n=1}^{3} V_{nx}(1 - \cos(n\phi)) \right)$$

$$V(\theta, \phi) = V_{CH3}(\text{Correction}(\phi)) \times (0.5)(1 - \cos(3\theta)) + V_{OH}(\phi)$$

where the values of the constants are listed in the Table below.

Table S3: Constants for the two-dimensional potential for the OH and CH$_3$ torsion in ethanol.

| Constant in Eq. (1) | Value (cm$^{-1}$) |
|---------------------|-------------------|
| $V_{1x}$            | 0.0653            |
| $V_{2x}$            | 0.000147          |
| $V_{3x}$            | 0.00827           |
| $V_{CH3}$           | 1208.4            |
| $V_{1OH}$           | 86.3              |
| $V_{2OH}$           | -4.37             |
| $V_{3OH}$           | 381.9             |
| $V_{4OH}$           | -32.7             |

The 1-D DVR results for the OH torsional potential have been shown in Fig. 8 of the
main text. As mentioned there, the only adjustable parameter is the moment of inertia for
the rotor, which was taken to be $2.7/(N_AV m_e)$. A 1-D DVR result for the CH$_3$ potential
is shown in Figure S3. The moment of inertia for the methyl rotor was taken here to be
$10.5/(N_AV m_e)$.

Given the 2D potential in Eq. (S1) and the parameters in Table S3, we can predict how
the OH torsion will vary as a function of the CH$_3$ torsional angle $\theta$, as shown in Fig. S4.
Not surprisingly, the barriers and the gauche conformation increase in energy as the methyl
rotates so that one CH bond eclipses the OH bond. The figure demonstrates substantial
interaction between the methyl and OH torsional motions.

Finally, we can also perform a 2-D DVR calculation$^2$ using the model 2-D potential. The
previously described moments of inertia were adjusted to obtain the best fit. Results are
shown in the Table in the main text.
Figure S2: Torsional potential (not fully relaxed) of the methyl rotor of TS1 (a) and TS2 (b) geometry of Ethanol.
Figure S3: 1-D DVR results for the CH$_3$ torsional potential, whose potential is shown in the blue curve. The energy levels are shown as dotted lines, while the wavefunctions for the lowest three levels are shown as solid red, green, and purple lines.

Figure S4: OH torsional potential for $\theta = 0$ and $\theta = 60$ degrees, normalized to have the same minimum.
Comparison of DVR and DMC torsional wavefunctions

Figure S5: Comparison of the ground state OH torsional wavefunctions as determined from Discrete Variable Representation calculation on a 1-D cut (red) and from Diffusion Monte Carlo calculations on the full-dimensional PES (blue). Note that both wavefunctions have substantial amplitude near 120°, the geometry of the gauche state.

Figure S6: Snapshots of OH torsional path.
DFT vs CCSD(T) PES Comparison

Table S4: Comparison of energetics (in cm$^{-1}$) between DFT PES$^3 (V_{LL})$ and CCSD(T) PES ($\Delta$-ML) relative to trans minimum energy.

| Geom.          | $V_{LL}$-PES$^a$ | $\Delta$-ML PES | Diff. |
|----------------|------------------|------------------|-------|
| Gauche         | 20               | 38               | 18    |
| TS1            | 377              | 342              | -35   |
| TS2            | 472              | 491              | 21    |
| $-$CH$_3$ Torsional Barrier | 1180            | 1174             | -6    |

$^a$ From Ref. 3.
Table S5: Comparison of harmonic frequencies (in cm$^{-1}$) between DFT PES$^3$ ($V_{LL}$) and CCSD(T) PES ($\Delta$-ML) of both trans and gauche isomers of Ethanol.

| Mode | Trans | Gauche |
|------|-------|--------|
|      | $V_{LL}$-PES$^a$ | $\Delta$-ML PES | Diff. | $V_{LL}$-PES$^a$ | $\Delta$-ML PES | Diff. |
| 1    | 237   | 242    | 5     | 267   | 268    | 1     |
| 2    | 269   | 273    | 4     | 279   | 278    | -1    |
| 3    | 417   | 417    | 0     | 422   | 425    | 3     |
| 4    | 820   | 817    | -3    | 804   | 804    | 0     |
| 5    | 896   | 909    | 13    | 882   | 895    | 13    |
| 6    | 1035  | 1055   | 20    | 1057  | 1075   | 18    |
| 7    | 1094  | 1115   | 21    | 1075  | 1094   | 19    |
| 8    | 1176  | 1181   | 5     | 1133  | 1144   | 11    |
| 9    | 1266  | 1284   | 18    | 1280  | 1290   | 10    |
| 10   | 1299  | 1302   | 3     | 1368  | 1375   | 7     |
| 11   | 1402  | 1403   | 1     | 1403  | 1406   | 3     |
| 12   | 1446  | 1454   | 8     | 1416  | 1424   | 8     |
| 13   | 1483  | 1488   | 5     | 1487  | 1490   | 3     |
| 14   | 1498  | 1500   | 2     | 1494  | 1496   | 2     |
| 15   | 1524  | 1530   | 6     | 1515  | 1519   | 4     |
| 16   | 2978  | 2995   | 17    | 2989  | 3007   | 18    |
| 17   | 3005  | 3029   | 24    | 3015  | 3020   | 5     |
| 18   | 3031  | 3036   | 5     | 3068  | 3089   | 21    |
| 19   | 3098  | 3120   | 22    | 3087  | 3108   | 21    |
| 20   | 3105  | 3126   | 21    | 3100  | 3121   | 21    |
| 21   | 3843  | 3862   | 19    | 3826  | 3845   | 19    |

$^a$ From Ref. 3.
Table S6: Comparison of harmonic frequencies (in cm$^{-1}$) between DFT PES$^3$ ($V_{LL}$) and CCSD(T) PES ($\Delta$-ML) of both eclipsed and syn TSs of Ethanol.

| Mode | $V_{LL}$-PES$^a$ | $\Delta$-ML PES | Diff. | $V_{LL}$-PES$^a$ | $\Delta$-ML PES | Diff. |
|------|-----------------|-----------------|-------|-----------------|-----------------|-------|
| 1    | 261$i$         | 267$i$         | 6$i$  | 336$i$         | 332$i$         | -4$i$ |
| 2    | 259            | 261            | 2     | 270            | 270            | 0     |
| 3    | 420            | 420            | 0     | 408            | 411            | 3     |
| 4    | 801            | 800            | -1    | 812            | 812            | 0     |
| 5    | 887            | 899            | 12    | 878            | 892            | 14    |
| 6    | 1036           | 1058           | 22    | 1044           | 1057           | 13    |
| 7    | 1087           | 1106           | 19    | 1079           | 1104           | 25    |
| 8    | 1126           | 1133           | 7     | 1182           | 1186           | 4     |
| 9    | 1275           | 1285           | 10    | 1292           | 1307           | 15    |
| 10   | 1360           | 1370           | 10    | 1306           | 1308           | 2     |
| 11   | 1397           | 1399           | 2     | 1405           | 1406           | 1     |
| 12   | 1423           | 1427           | 4     | 1440           | 1446           | 6     |
| 13   | 1481           | 1485           | 4     | 1491           | 1493           | 2     |
| 14   | 1498           | 1500           | 2     | 1502           | 1507           | 5     |
| 15   | 1517           | 1522           | 5     | 1531           | 1534           | 3     |
| 16   | 3003           | 3020           | 17    | 3010           | 3015           | 5     |
| 17   | 3023           | 3028           | 5     | 3013           | 3027           | 14    |
| 18   | 3035           | 3059           | 24    | 3034           | 3054           | 20    |
| 19   | 3091           | 3112           | 21    | 3082           | 3103           | 21    |
| 20   | 3102           | 3122           | 20    | 3088           | 3109           | 21    |
| 21   | 3875           | 3896           | 21    | 3853           | 3872           | 19    |

$^a$ From Ref. 3.
References

(1) Kirschner, K. N.; Heiden, W.; Reith, D. Small Alcohols Revisited: CCSD(T) Relative Potential Energies for the Minima, First- and Second-Order Saddle Points, and Torsion-Coupled Surfaces. *ACS Omega* **2018**, *3*, 419–432.

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