Electronic Supplementary Information: For Review Purpose

Accurate entropy calculation for large flexible hydrocarbons using multi-structural 2-dimensional torsion method

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Note: this ESI is about the details of applying MS-2DT method to treat the oxygenate and the transition state containing H-bonds.

We testified the applicability of MS-2DT method for methyl butanoate (MB) and one of its transition state (MB-TS2). For MB molecule, it has five torsions including two terminal methyl groups. Therefore, only three torsions (as shown in Figure S1) are considered to generate the initial conformer space. A standard MS-T treatment generates 27 initial structures, and the MS-2DT treatment also generates 27 initial structures. Although the same number of initial structures, the distinguished structures located by MS-T method is 18 (including the mirror structures), while the distinguished structures located by MS-2DT is 14.

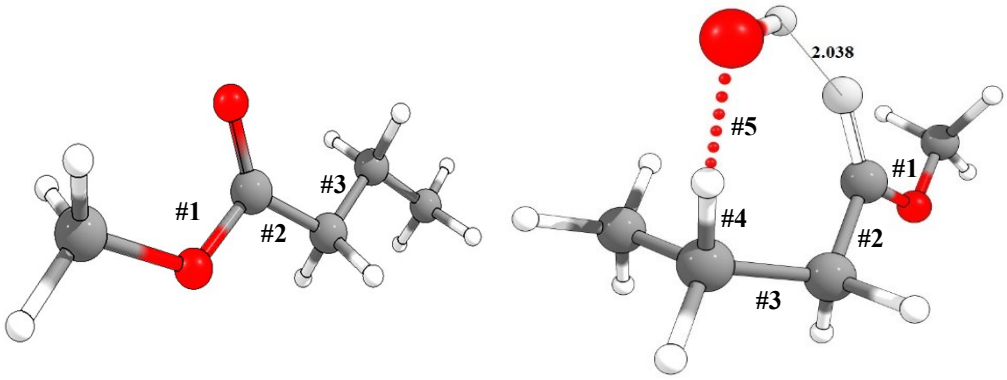

Figure S1. The torsions of methyl butanoate and one of its transition state

For the transition state, it has 7 torsions and two of them are terminal methyl groups. Therefore, the number of initial structures generated by MS-T calculation is 3^5=243, while the number of initial structures generated by MS-2DT is $C_5^2 \cdot 3^2 = 90$. Clearly, a lot of computational efforts can be saved for the initial conformer search. The MS-T method locates 58 distinguished conformers, the MS-2DT method locates 26 distinguished conformers.

Table S1 listed the entropies of MB and MB-TS2 calculated by MS-T and MS-2DT methods. We can see that the MS-2DT can predicts entropies of complex systems with comparable accuracy to MS-T method. Besides, the MB-TS2 containing H-bond is difficult to be treated by conventional 1D-HR method, however, it's can be well treated by MS-2DT method. In this sense, we believe the MS-2DT method is applicable to complicated systems.

Table S1. Entropies of MB and MB-TS2 calculated by MS-T and MS-2DT methods (unit in cal·mol^{-1}·K^{-1}).

T (K)	MB		MB-TS2	
	MS-T	MS-2DT	MS-T	MS-2DT
298	94.093	95.913	102.555	101.551
200	82.717	84.906	88.908	87.626
250	88.754	90.746	95.988	94.82
300	94.309	96.122	102.828	101.83
350	99.564	101.22	109.623	108.776
400	104.611	106.13	116.342	115.575
450	109.492	110.889	122.857	122.102

500	114.223	115.513	129.067	128.284
600	123.262	124.376	140.477	139.618
700	131.771	132.744	150.716	149.806
800	139.786	140.644	160.048	159.116
900	147.347	148.109	168.667	167.729
1000	154.49	155.17	176.698	175.763
1100	161.248	161.856	184.224	183.299
1200	167.651	168.195	191.307	190.395
1300	173.726	174.213	197.995	197.098
1400	179.497	179.932	204.327	203.448
1500	184.987	185.376	210.335	209.475
1600	190.218	190.565	216.049	215.208
1700	195.207	195.516	221.492	220.671
1800	199.973	200.249	226.686	225.886
1900	204.532	204.777	231.652	230.872
2000	208.9	209.117	236.406	235.646