

## A Density Functional Study of Methanol Clusters

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**Abstract:** The potential energy surfaces of methanol clusters,  $(\text{CH}_3\text{OH})_n$ ,  $n = 2-12$ , have been studied using density functional theory at the B3LYP/6-31G(d) and higher levels of theory. Cyclic clusters in which  $n$  methanol molecules are joined in a ring structure formed by  $n$  hydrogen bonds are shown to be more stable than structures of the same number of methanol molecules where one or more methanol molecules are outside the ring and are hydrogen-bonded to oxygens of methanols in rings of  $n - 1$ ,  $n - 2$ , and so forth. So-called chain structures are generally even less stable. Furthermore, the hydrogen-bonding energy per methanol molecule of the  $n$ -ring clusters is shown to converge to an asymptotic value of about 27 kJ/mol at B3LYP/6-311+G-(d,p)//B3LYP/6-31G(d) after five to six methanols are included in the cluster. As expected, there are many minima on the potential energy surfaces of the methanol clusters, the number increasing rapidly with  $n$ . A cyclic cluster of five to six methanol molecules appears to be sufficient to mimic liquid behavior as far as vibrational frequencies are concerned.

### Introduction

Like water, liquid methanol displays anomalous behavior, including a high boiling point, due to hydrogen bonding. Unlike water, whose bulk properties are entirely governed by hydrogen bonding, methanol has both hydrogen bonding and hydrophobic interactions. The latter are due to the presence of the methyl group, which imposes a constraint on the hydrogen-bonding network in condensed phases.

It is well-known that each oxygen in water is able to act as a donor for two hydrogen bonds and as an acceptor for two hydrogen bonds; therefore, in the solid state, the coordination number of oxygen is four. Liquid water is much less ordered than the solid, but nonetheless, the “structure” and properties are dominated by hydrogen bonding. The oxygen atom in methanol is limited to being a single hydrogen-bond donor. In principle, each oxygen in methanol may be an acceptor for two hydrogen bonds, but it is much more probable that a given oxygen atom will be an acceptor

for only one hydrogen bond. The latter point is supported by experimental studies of crystalline methanol which clearly show that the methanol molecules are connected by hydrogen bonds to form one-dimensional structures.<sup>1,2</sup> This simple difference between methanol and water has important consequences for the structure of liquid methanol.

The investigation of the structure of liquid methanol has a long history and remains an active research topic.<sup>3,4</sup> In his classic treatise, Pauling<sup>5</sup> proposed that the molecules in liquid methanol form cyclic hexamer structures. Numerous experimental and theoretical studies have been designed to test Pauling’s hypothesis. Sarkar and Joarder<sup>6</sup> have provided support on the basis of an analysis of earlier neutron diffraction<sup>7,8</sup> and X-ray scattering<sup>9,10</sup> experiments. Recent resonant soft X-ray emission spectroscopy experiments by Kashtanov et al.,<sup>11</sup> supported by density functional theory (DFT), suggest that liquid methanol consists of combinations of rings and chains of methanol molecules linked with hydrogen bonds and is dominated by hexamers and octamers. Wilson et al.<sup>12</sup> have used X-ray absorption spectroscopy and DFT-computed spectra to arrive at very similar conclusions. Thus, there appears to be a convergence of conclusions from experimental studies on the structure of liquid methanol.

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Additional information on the electronic and thermodynamic properties of liquid methanol has been obtained from a variety of experimental studies.<sup>13–19</sup>

Many theoretical studies of liquid methanol have been reported. The early Monte Carlo work of Jorgensen,<sup>20</sup> the classical molecular dynamics (MD) simulation of Haughney et al.,<sup>21</sup> and the latest ab initio MD simulations<sup>22–24</sup> all favor the existence of chains, but there is no agreement on the average chain length. It has been suggested<sup>11</sup> that MD simulations based on potentials derived from the methanol dimer do not predict ring structures because of significant differences between the polarization in the dimer and larger rings. Potentials that provide a better description of hydrogen bonding in ring structures are required for future MD simulations.

The red-shifted hydroxyl-stretching mode in liquid methanol has been the subject of several studies,<sup>25,26</sup> including the first ab initio MD simulation of liquid methanol,<sup>27</sup> while others have attempted to account for thermodynamic properties.<sup>28–33</sup> Many of the studies have employed hybrid quantum mechanical/molecular mechanical (QM/MM) methods.<sup>34,35</sup> Despite the many MD and QM/MM studies of liquid methanol, it is surprising that so few studies by conventional electronic structure methods of methanol clusters in the gas phase have been published. The most comprehensive study to date is the work of M6 et al.<sup>36</sup> on the methanol trimer, in which high-level calculations showed that the most favorable structure is a ring with one methyl group above the ring and two below the ring. Mandado et al.<sup>37</sup> have studied cooperative effects in the methanol trimer. Vener and Sauer<sup>38</sup> have reported an MP2 and B3LYP study of two cyclic isomers of the methanol tetramer. B3LYP/6-31+G(d) calculations on clusters as large as the octamer have been reported by Ludwig;<sup>39</sup> by combining the DFT calculations with a quantum cluster equilibrium model, he concludes that liquid methanol is dominated by cyclic and/or lasso structures. El-Shall et al.<sup>40</sup> have reported Monte Carlo simulations of  $(\text{CH}_3\text{OH})_n$ ,  $n = 2–9$ , clusters.

Despite the extensive literature on the structures of methanol clusters, only the trimer surface has been explored thoroughly.<sup>36</sup> For the methanol tetramer, we have located 12 stationary points on the surface corresponding to minima, whereas only two have been reported previously.<sup>38</sup> In this paper, we use a reliable level of electronic structure theory to study methanol clusters as large as the dodecamer,  $(\text{CH}_3\text{OH})_{12}$ . Our goal is to complement earlier work on clusters and to stimulate MD simulations with improved potentials.

## Nomenclature

We have considered various types of clusters.

(i) A cluster of  $n$  methanol molecules,  $(\text{CH}_3\text{OH})_n$ , where all  $n$  molecules are joined in a single ring structure with  $n$  hydrogen bonds, is termed an  $nr$ - $n$ mer, for example, the methanol 6r-hexamer or the 6r-hexamer.

(ii) Systems which contain a ring and branches from that ring, where the branches are  $x$  methanol “monomers” hydrogen-bonded to an oxygen in the ring, are called  $((n - x)r + xm)$ - $n$ mer; for example, a hexamer formed from a

tetramer ring with two single methanol branches from the ring is called a  $(4r + 2m)$ -hexamer.

(iii) We have also studied a few examples in which the branch is two or more methanols in length; that is, the branch is a “dimer”, “trimer”, and so forth; these are called  $((n - x)r + x/2 d)$ - $n$ mer, and so forth, as in the case of a pentamer formed from a three-membered ring with one dimer branch,  $(3r + 1d)$ -pentamer.

(iv) When there is reason to do so for clarification, we have used  $u$  and  $d$  as a subscript for up and down, respectively, to indicate the direction of the methyl groups relative to the (approximately) planar arrangement of the O–H bonds participating in the rings; thus, the lowest-energy trimer ring structure has a  $udu$  arrangement, as noted previously by M6 et al.,<sup>36</sup> and is called the  $3r_{udu}$ -trimer.

(v) Sometimes, to distinguish between different “isomers”, we have had to clarify where the branching occurs, as in  $(4r_{uddd} + 1m_{d2})$ -pentamer. This notation means that the single methanol branch on the four-membered ring of the pentamer occurs at the second “down” methanol in the ring.

(vi) Note also that some structures, in addition to normal H bonds, have a weak interaction between the O of a hydroxyl group and the H of a nearby methyl group. When this occurs, it is indicated, as in the  $(3r + 1m_{O\cdots HC})$ -tetramer. In this structure, the methanol outside the three-membered ring in a sense straddles the ring, via both a normal H bond and the extra weak  $\text{O}\cdots\text{HC}$  interaction. The  $\text{O}\cdots\text{HC}$  interaction closes a ring; the smallest example was described for the trimer by Mandado et al.<sup>37</sup>

(vii) Finally, we have considered structures where the methanols are H-bonded into chains; these are referred to as  $nc$ - $n$ mers, for example, the 6c-hexamer, and all of these have one or more inter- $\text{O}\cdots\text{HC}$  actions, which are either “tight” as for the trimer  $\text{O}\cdots\text{HC}$  ring of Mandado et al.<sup>37</sup> or “loose” when it is a tetramer that is closed by the  $\text{O}\cdots\text{HC}$  interaction.

Clearly, as the value of  $n$  increases, the number of “isomers” for an  $n$ mer grows enormously; branched chain structures could exist, and so on. We have not attempted to optimize all possible structures for any  $n$ mers except the tetramers.

## Computational Methods

All density functional theory calculations reported herein were carried out using the Gaussian 03 suite of programs.<sup>41</sup> The geometry optimizations on the  $(\text{CH}_3\text{OH})_n$ ,  $n = 2–12$ , clusters were performed using the B3LYP functional and the 6-31G(d) basis set. The B3LYP functional is composed of Becke’s three-parameter hybrid exchange functional (B3),<sup>42,43</sup> as implemented in Gaussian 03,<sup>44</sup> and the correlation functional of Lee, Yang, and Parr (LYP).<sup>45</sup> Harmonic vibrational frequencies and zero-point vibrational energy (ZPVE) corrections were calculated at the same level of theory. A few additional calculations with larger basis sets were carried out as a check on the effects of basis set truncation. Relative energies were determined by single-point studies with the B3LYP functional and the 6-311+G(d,p) basis set, as discussed below.

**Table 1.** Selected Bond Lengths from Optimized Geometries of Methanol and Methanol Trimer Global Minimum Energy Structures, as Obtained with Various Basis Sets

level	bond lengths (Å) <sup>a</sup>					
	methanol		3 <sub>trimer</sub>			
	C–O	O–H	O···O	C–O	O–H	O···H
B3LYP/6-31G	1.452	0.978	2.634	1.449	1.002	1.721
			2.641	1.447	1.002	1.736
			2.627	1.447	1.001	1.717
			(2.634)	(1.448)	(1.002)	(1.725)
B3LYP/6-31G(d)	1.418	0.969	2.740	1.423	0.986	1.825
			2.753	1.421	0.987	1.844
			2.741	1.421	0.986	1.829
			(2.744)	(1.422)	(0.986)	(1.833)
B3LYP/6-31G(d,p)	1.418	0.965	2.743	1.422	0.982	1.833
			2.756	1.420	0.983	1.852
			2.745	1.421	0.982	1.836
			(2.748)	(1.421)	(0.982)	(1.840)
B3LYP/6-31+G(d)	1.425	0.969	2.765	1.426	0.984	1.863
			2.778	1.424	0.984	1.886
			2.766	1.424	0.983	1.866
			(2.770)	(1.425)	(0.984)	(1.872)
B3LYP/6-31+G(d,p)	1.426	0.965	2.770	1.425	0.980	1.873
			2.782	1.424	0.901	1.986
			2.771	1.424	0.979	1.876
			(2.774)	(1.424)	(0.953)	(1.912)
B3LYP/6-311+G(d,p) <sup>b</sup>	1.424	0.961	2.765	1.424	0.976	1.876
			2.778	1.422	0.976	1.874
			2.770	1.422	0.975	1.902
			(2.771)	(1.423)	(0.976)	(1.884)
MP2/6-311+G(d,p) <sup>c</sup>	1.421	0.959	2.761	1.422	0.972	1.879
			2.776	1.421	0.972	1.896
			2.763	1.421	0.973	1.867
			(2.767)	(1.421)	(0.972)	(1.881)

<sup>a</sup> Average values for the 3<sub>trimer</sub> bond lengths are in parentheses. <sup>b</sup> From Mó et al.<sup>36</sup> <sup>c</sup> From Mó et al.<sup>36</sup> Supporting Information.

## Results and Discussion

### A. Choice of the Computational Method and Basis Set.

Given that our goal was to study larger clusters than those studied previously, our first objective was to identify an appropriate level of theory. For this purpose, we used the study of the methanol 3<sub>trimer</sub> potential energy surface by Mó et al.<sup>36</sup> as a reference. Our target was a basis set which yields bond lengths that agree to within 0.01 Å with the Mó et al. calculations and intermolecular distances that agree to within 0.05 Å. We assumed that the four internuclear distances,  $r(\text{O}\cdots\text{O})$ ,  $r(\text{C}-\text{O})$ ,  $r(\text{O}-\text{H})$ , and  $r(\text{O}\cdots\text{H})$ , were sufficient comparators for this purpose. Furthermore, our goal was to find a level of theory that yielded dissociation energies that agree to within 5 kJ/mol of the Mó et al. calculations for the trimer.

Before entering into a detailed discussion of the choice of the computational method and basis set, it should be noted that it would be desirable to use the MP2 method with a fairly large basis set, such as the aug-CC-pVDZ basis set. Unfortunately, with our computational facilities, we cannot get beyond the pentamer with MP2/aug-CC-pVDZ. Given that our goal is to be able to include the dodecamer and to treat all clusters at a uniform level, we were forced to compromise. Methods based on density functional theory

offer the best alternative. It is well-known, however, that DFT methods fail to provide accurate descriptions of weak interactions. Such problems are most severe for dispersion-bound systems. But it is also well-established<sup>46,47</sup> that some of the commonly used functionals provide an adequate description of relatively strong hydrogen-bonded interactions, such as the  $\text{O}-\text{H}\cdots\text{O}$  interactions that are present in liquid methanol.

For the purposes of the following discussion, we define the term “dissociation energy” as

$$D_0 = nE(\text{CH}_3\text{OH}) - E(n\text{mer}) \quad n = 2-12$$

where the terms  $E(n\text{mer})$  and  $E(\text{CH}_3\text{OH})$  include the corresponding ZPVE (unscaled) but not the basis set superposition error or thermal corrections. (Our aim was to observe trends as the size of the methanol cluster increases, rather than to attain the experimental accuracy sought by Mó et al. for the small trimer system.)

Table 1 lists the key geometrical parameters of the optimized geometries of the 3<sub>trimer</sub> structure obtained with the B3LYP method and the 6-31G, 6-31G(d), 6-31G(d,p), 6-31+G(d), and 6-31+G(d,p) basis sets; these are compared with the same parameters obtained by Mó et al., who used

**Table 2.** Dissociation Energies ( $D_0$ ) for the Methanol  $3r_{udu}$ -Trimer

level of theory	methanol		3r <sub>udu</sub> -trimer		D <sub>0</sub> (kJ/mol)
	E (au)	ZPVE (au)	E (au)	ZPVE (au)	
Full Optimization Study					
B3LYP/6-31G	−115.679 50	0.051 07	−347.086 91	0.159 86	109.6
B3LYP/6-31G(d)	−115.714 41	0.051 48	−347.181 74	0.160 99	83.9
B3LYP/6-31G(d,p)	−115.723 96	0.051 41	−347.209 46	0.160 46	82.3
B3LYP/6-31+G(d)	−115.725 19	0.051 31	−347.205 02	0.160 05	61.2
B3LYP/6-31+G(d,p)	−115.734 87	0.051 23	−347.232 26	0.159 42	57.6
B3LYP/6-311+G(d,p)	−115.764 94	0.051 05	−347.322 09	0.158 82	56.7
single point, B3LYP/6-31G(d) geometry					
B3LYP/6-31G(d)	−115.714 41	0.051 48	−347.181 74	0.160 99	83.9
B3LYP/6-31G(d,p)	−115.723 94	0.051 48	−347.209 44	0.160 99	81.6
B3LYP/6-31+G(d)	−115.725 06	0.051 48	−347.204 07	0.160 99	58.6
B3LYP/6-31+G(d,p)	−115.734 74	0.051 48	−347.231 09	0.160 99	53.4
B3LYP/6-311+G(d,p)	−115.764 78	0.051 48	−347.320 46	0.160 99	51.4
Mó, Yáñez and Elguero <sup>a</sup>					
B3LYP/6-311++G(3df,2p)//6-311+G(d,p)	−115.773 09	0.051 04	−347.343 30	0.158 80	48.2

<sup>a</sup> From Mó et al.<sup>36</sup> Supporting Information, except *without* thermal energy, BSSE corrections, or scaling of ZPVE, to allow direct comparison with our data.

B3LYP/6-311+G(d,p) and MP2/6-311+G(d,p) optimized geometries. The B3LYP/6-31G structural parameters agree poorly with the B3LYP/6-311+G(d,p) results. The addition of d-type polarization functions on the heavy atoms eliminates most of the error, while further improvement in the basis set leads to more modest incremental improvements. The B3LYP/6-31G(d) bond lengths for the methanol monomer are within 0.01 Å of the B3LYP/6-311+G(d,p) ones of Mó et al.; for the trimer, C–O and O–H bonds are similarly within 0.01 Å. The intermolecular distances vary to a slightly greater extent: the B3LYP/6-31G(d) calculations yield shorter intermolecular distances, for example, an average O···H bond of 1.83 Å compared to the B3LYP/6-311+G(d,p) result of 1.88 Å, and an average O···O distance of 2.74 Å compared to 2.77 Å. In view of these observations and in order to make large clusters accessible with our computational facilities, we conclude that the B3LYP/6-31G(d) optimization of geometries of methanol clusters, which yields parameters within 0.01 Å for bond lengths and 0.05 Å for intermolecular distances, is adequate.

Table 2 lists the dissociation energy obtained for the  $3r_{udu}$ -trimer global minimum energy structure with each of the various basis sets listed. Given that we have aimed to attain dissociation energies for this trimer that agreed within 5 kJ/mol with those obtained in the comprehensive study of Mó et al., we have used single-point energies from the B3LYP/6-311+G(d,p) level of theory, calculated with the B3LYP/6-31G(d) geometry and frequency. This yields a stabilization energy of 51.4 kJ/mol for the trimer, which compares well with the 48.2 kJ/mol obtained by Mó et al. who used a much larger basis set, B3LYP/6-311++G(3df,2p), for their single-point study, together with a geometry optimized with B3LYP/6-311+G(d,p). (Note: the Mó et al. paper reports results calculated by including thermal energies, scaled ZPVE, and BSSE corrections; we have recalculated their data without these corrections, so that their results may be directly compared to ours.)

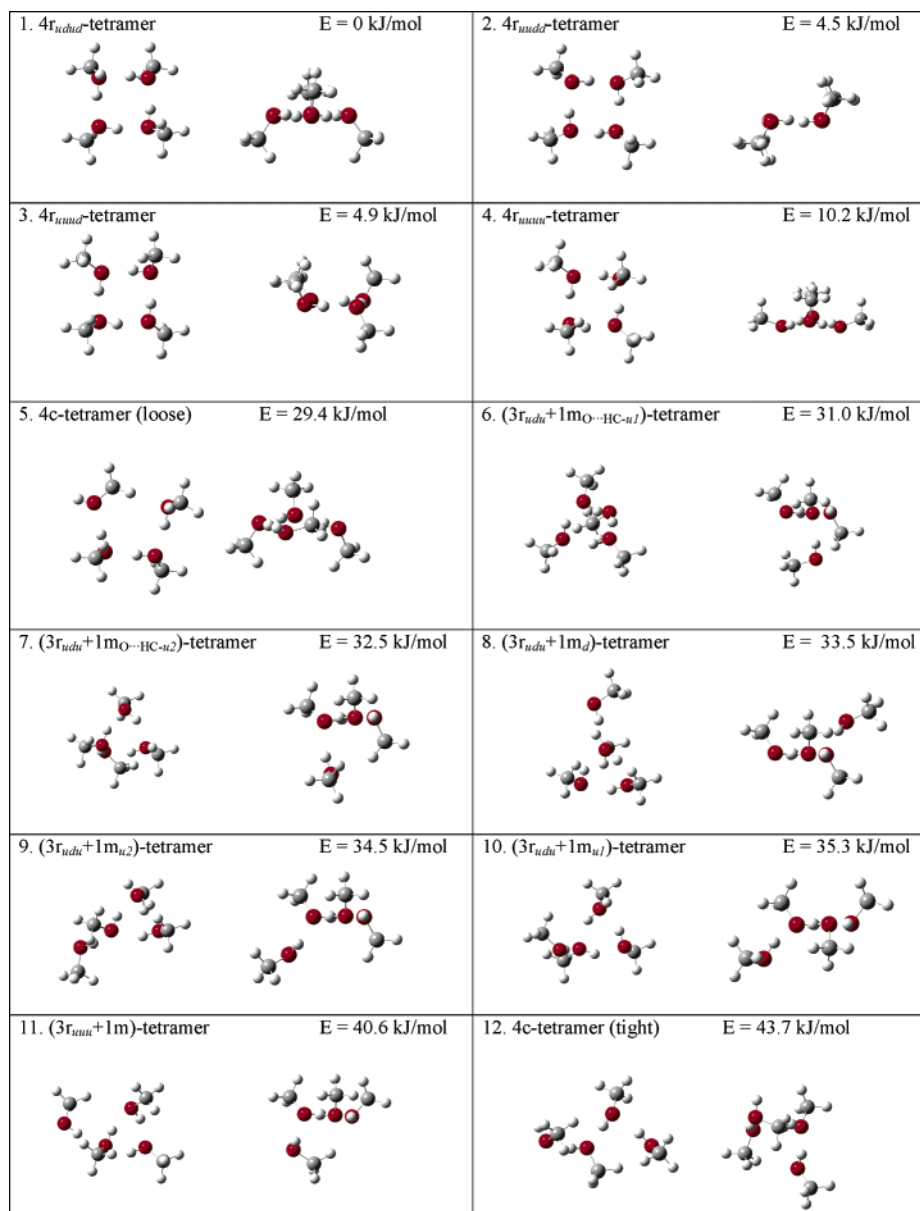
**B. Geometries of the  $n$ mers.** As noted above, the number of possible “isomers” for an  $n$ mer increases rapidly with  $n$ . To illustrate this, Figure 1 shows the structures of the 12 tetramers, both “top” and “side” views, for which minima (no imaginary frequencies) were found on the B3LYP/6-31G(d) surface. B3LYP/6-311+G(d,p) single-point energies of each of the conformers (including B3LYP/6-31G(d) ZPVE), relative to that of the lowest-energy one, are given in kilojoules per mole. The complete set of structures and geometrical parameters is available as Supporting Information.

**C. Dissociation Energies of the Methanol Clusters.** In Figure 2 are plotted the dissociation energies [B3LYP/6-311+G(d,p) single-point energies obtained with B3LYP/6-31G(d) geometries and ZPVE] per mole of methanol for the various ( $n = 1$ –12) methanol clusters. The lowest-energy species is plotted for each type of ring for a given  $n$ mer. For example, while four 4r-tetramer structures were found (*udud*, *uudd*, *uuud*, and *uuuu*), only the energy for the *udud* structure appears on the plot. Similarly, the lowest energy of the six (3r+1m)-tetramer structures is given, and so forth. There are many points worth noting.

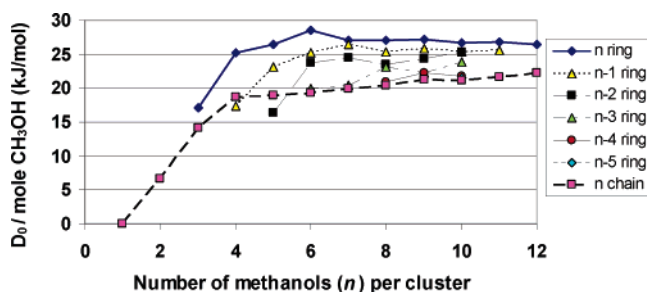
(1) Clearly there is an increase in the dissociation energy per mole of methanol as the number of methanol molecules in the cluster increases to about six; that is, the larger clusters are more stable than the smaller ones until the cluster reaches about six methanol molecules. At that point, the  $D_0$ /mole of methanol essentially levels off.

(2) The curve for the largest rings of a given  $n$  in Figure 2 is not smooth as  $n$  increases. This may be due to the possibility that the lowest-energy ring species was not found in each case. The potential energy surface is very flat for the different conformers of the clusters, as has been noted by Mó et al. for the trimer,<sup>36</sup> and it is quite possible that, despite many searches in each case, the global minimum energy structure was not found for some of these clusters.



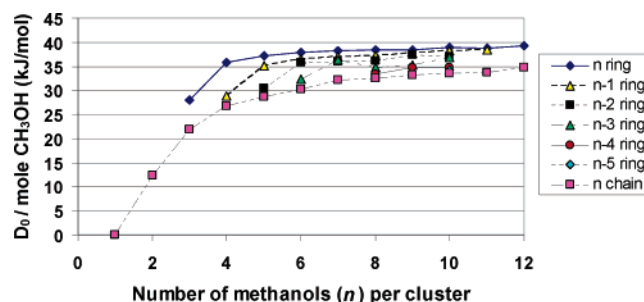


**Figure 1.** Minimum energy structures for the methanol tetramers. B3LYP/6-311+G(d,p) single-point energies, including B3LYP/6-31G(d) ZPVE, relative to that of the global minimum energy structure are indicated (kJ/mol).



**Figure 2.** Dissociation energies of methanol clusters per mole of methanol as a function of the number of methanol molecules, at the B3LYP/6-311+G(d,p)//6-31G(d) level with B3LYP/6-31G(d) ZPVE included.

Another explanation may be the fact that the energies were obtained with a larger basis set than the geometries and ZPVE. When B3LYP/6-31g(d) energies from optimized geometries and ZPVE are used, the curve is somewhat



**Figure 3.** Dissociation energies of methanol clusters per mole of methanol as a function of the number of methanol molecules, at the B3LYP/6-31G(d) level with ZPVE corrections included.

smoother (Figure 3). A third possibility is that the fluctuations may be real and may reflect, for example, that the 6r-hexamer, as predicted long ago by Pauling,<sup>5</sup> is the most stable cyclic methanol cluster.

**Table 3.** Dissociation Energy of Pentamer Clusters per Mole of Pentamer and per Mole of Methanol at B3LYP/6-311+G(d,p)//B3LYP/6-31G(d)

cluster		$E$ au	ZPVE au	$\Delta E$ conf <sup>a</sup> kJ/mol	$D_0$ kJ/mol	$D_0$ / mole CH <sub>3</sub> OH kJ/mol
1	5r <sub>ududu</sub> -pentamer “planar”	−578.885 23	0.268 26	0	132	26
2	5r <sub>uuuu</sub> -pentamer	−578.884 88	0.268 15	0.91	132	26
3	5r <sub>ududu</sub> -pentamer “envelope”	−578.883 39	0.268 97	4.83	126	25
4	(4r <sub>udud</sub> + 1m)-pentamer	−578.879 86	0.269 28	14.10	116	23
5	(4r <sub>udud</sub> + 1m <sub>0</sub> •HC)-pentamer	−578.879 31	0.269 20	15.54	114	23
6	(4r <sub>uddd</sub> + 1m <sub>1</sub> )-pentamer	−578.877 50	0.268 45	20.30	112	22
7	(4r <sub>uddd</sub> + 1m)-pentamer	−578.877 44	0.268 55	20.46	111	22
8	(4r <sub>uddd</sub> + 1m <sub>d2</sub> )-pentamer	−578.877 38	0.268 27	20.60	112	22
9	(4r <sub>uddd</sub> + 1m <sub>d3</sub> )-pentamer	−578.876 86	0.268 55	21.97	110	22
10	(4r <sub>uuuu</sub> + 1m)-pentamer	−578.874 72	0.268 40	27.58	105	21
11	(3r <sub>udu</sub> + 1d)-pentamer	−578.870 75	0.268 78	38.00	93	19
12	5c-pentamer (loose)	−578.870 29	0.267 81	39.22	94	19
13	5c-pentamer (tight)	−578.869 58	0.267 90	41.08	92	18
14	(3r <sub>udu</sub> + 2m)-pentamer	−578.865 73	0.268 01	51.19	82	16

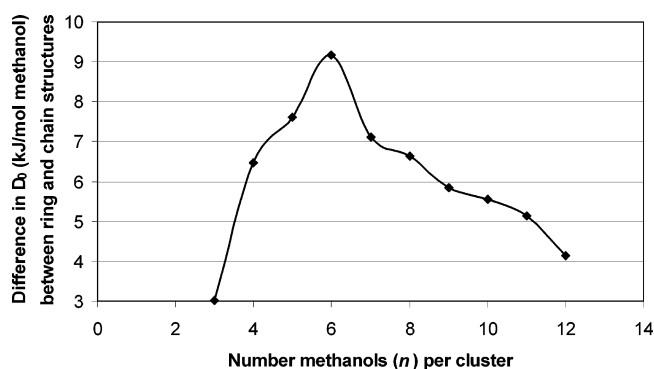
<sup>a</sup>  $\Delta E$  conf =  $(E + \text{ZPVE})_{\text{conformer}} - (E + \text{ZPVE})_{\text{minimum\_energy\_structure}}$  in kJ/mol.

(3) Both Figures 2 and 3 indicate that the maximum dissociation energy per mole of methanol for a cluster of  $n$  methanol molecules is obtained when the clusters contain all  $n$  molecules in a single ring. This is not surprising, because the  $n$ -ring clusters have the greatest opportunity for H bonding, with each methanol molecule acting as both donor and acceptor, hence,  $n$  donors and  $n$  acceptors. For example, consider the data in Table 3, which lists the  $D_0$  for various pentamer clusters. Three different 5r-pentamer structures with zero imaginary frequencies were located; the “planar” one, in which the hydroxyl groups are approximately in a plane with the methyl groups alternating up and down, *ududu*, is the lowest-energy structure found. The three 5r-pentamer structures have  $D_0$  in the vicinity of 126–132 kJ/mol of pentamer (25–26 kJ/mol of methanol). With smaller ring structures, the dissociation energies are progressively lower. The (4r + 1m)-pentamer structures have  $D_0$  ranging from 105 to 116 kJ/mol of pentamer (21–23 kJ/mol of methanol); in this case, there are  $n$  donors but only  $n - 1$  acceptor H bonds. The (3r + 1d)-pentamer has  $D_0$  equal to 93 kJ/mol of pentamer (19 kJ/mol of methanol), while the (3r + 2m)-pentamer structure has a  $D_0$  of 82 kJ/mol of pentamer (16 kJ/mol of methanol). The pentamer chain has  $D_0$  equal to 92–94 kJ/mol of pentamer (18–19 kJ/mol of methanol). Similar trends were noted for all other clusters.

4. The data illustrated in Figure 2, which are based on B3LYP/6-311+G(d,p) single-point energies, show that the dissociation energies per mole of methanol for the  $n$ mers converge to a value of about 27 kJ/mol of methanol. [In Figure 3, the energies converge to about 40 kJ/mol for the B3LYP/6-31G(d) energies. A major effect of the larger basis set is to lower the calculated dissociation energies, as is also evident from the basis set study shown in Table 2.]

5. The “loose” chain structures are more stable than trimer ring structures, which have strain. For example, for the pentamers, the loose 5c-pentamer has a higher  $D_0$  than both the (3r + 2m)-pentamer and the (3r + 1d)-pentamer.

6. As  $n$  increases, the difference in  $D_0$  per mole of methanol between the lowest-energy ring structure for a

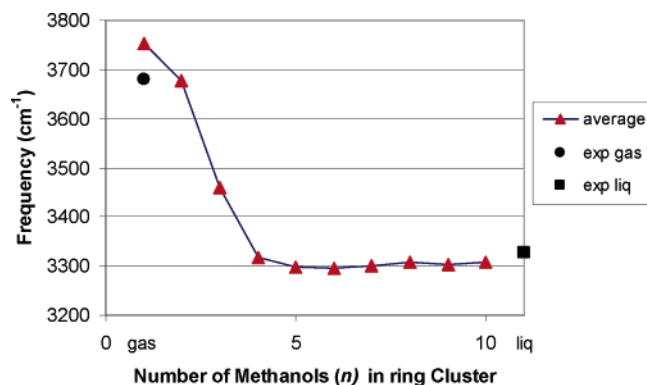


**Figure 4.** Difference in dissociation energies in kJ/mol of methanol [B3LYP/6-311+G(d,p)//B3LYP/6-31G(d)] between ring structures as a function of the number of methanols in the cluster.

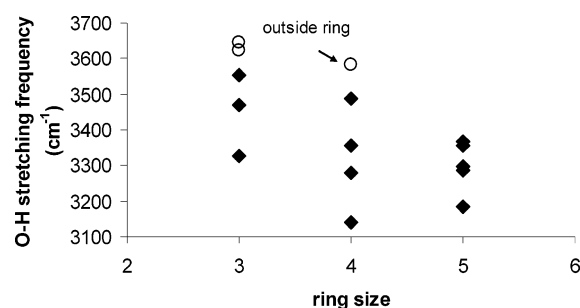
given  $n$  and the lowest-energy chain structure initially increases to a maximum at  $n = 6$  then decreases steadily, as illustrated in Figure 4. Thus, the 6r-hexamer is substantially more stable than the 6c-hexamer, but beyond that, the  $D_0$  per mole of methanol for the chain structures appears to be approaching those of the ring structures.

**D. Vibrational Frequency Shifts.** Figure 5 is a plot of the average O–H vibrational frequency as a function of the number of methanols in the ring structures. (Average values were used, because the  $n$ mers have  $n$  O–H stretching absorptions.) It is well-known that gaseous methanol has a higher vibrational frequency for the O–H stretch than liquid methanol.<sup>47</sup> Clearly, even with the small basis set used in this study [6-31G(d)], the O–H vibrational frequency drops as the number of methanols in the cluster increases. The minimum frequency is essentially attained when there are five methanols in the ring, which provides further evidence to support the suggestion that five or six hydrogen-bonded methanols are sufficient to mimic liquid behavior.

Another observation from the O–H stretch frequency data is that stretches associated with methanols that are outside the ring have higher frequencies than those within the ring.



**Figure 5.** Average B3LYP/6-31G(d) O–H vibrational frequencies ( $\text{cm}^{-1}$ ) for the methanol ring clusters as a function of  $n$ , compared to the experimental values in the gas and liquid<sup>46</sup> phases.



**Figure 6.** O–H stretching frequencies for three of the pentamer clusters as a function of the number of methanols within the ring. The structures are the lowest-energy ones in each of the respective groups, that is, the  $(3r_{udu} + 2m)$ -pentamer,  $(4r_{udud} + 1m)$ -pentamer, and  $5r_{ududu}$ -pentamer species.

Figure 6 shows the O–H stretching frequencies as a function of the number of methanol molecules within a ring for three pentamer clusters (the  $5r_{ududu}$ -pentamer, the  $(4r_{udud} + 1m)$ -pentamer, and the  $(3r_{udu} + 2m)$ -pentamer). In each case, the stretch associated with the methanol(s) with only donor H bonds has a significantly higher stretching frequency.

## Conclusions

The potential energy surfaces of methanol clusters are very flat. Our computational study of a series of  $(\text{CH}_3\text{OH})_n$  clusters, where  $n = 2\text{--}12$  methanol molecules, indicates that there are increasing numbers of minimum energy structures (no imaginary vibrational frequencies) as  $n$  increases. Furthermore, our study suggests that the dissociation energy per mole of methanol increases as  $n$  increases, up to about five to six methanols. Beyond that, the  $D_0$ /mole of methanol remains approximately constant at about 27 kJ/mol for B3LYP/6-311+G(d,p)/B3LYP/6-31G(d) energies, though this value is likely to be lower at a higher level of theory. Ring clusters of  $n$  molecules are more stable than branched-ring and chain ones; however, the difference in  $D_0$ /mole of methanol between ring and chain structures decreases as the value of  $n$  increases beyond six methanol molecules. On the basis of the results shown in Figures 2 and 3, it would appear that pentamer or hexamer structures approximate the bulk liquid behavior. This is supported by the results of O–H

vibrational energies (Figure 5). It would be interesting to know if a significantly higher level of theory would yield the same value, that is, that five to six methanol molecules in a cluster is sufficient to mimic liquid behavior.

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**Supporting Information Available:** Archive entries for all geometry optimizations of the structures discussed in this paper are available free of charge via the Internet at <http://pubs.acs.org>.

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