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Ab initio molecular analysis of dimethyl ether dimer. Thermodynamic properties

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Abstract. The potential surface of dimethyl ether dimer was subjected to an ab initio study at the second-order Møller–Plesset/6-31+G** level. The initial configurations used in the optimizations were chosen on the basis of a chemical criterion or compiled from the literature. Five different minima were identified and were confirmed by frequency calculations. Accurate characterization of the potential surface of the dimer entails considering electron correlation as several minima that are not exposed by Hartree–Fock/6-31+G** computations. Also, various thermodynamic properties of the minima were determined from their harmonic frequencies.

Key words: Dimethyl ether dimer – Intermolecular
Ab initio – Thermodynamic properties

1 Introduction

In recent years, a number of studies based on the use of ab initio methods to analyse the properties of dimers involving hydrogen bonds between protons and oxygen atoms in carbonyl or carboxyl groups have been carried out [1–4]. By contrast, studies of this type on clusters involving the ether group are much scantier. To our knowledge, no ab initio study of the dimers of the simplest possible ether (dimethyl ether) appears to have been reported. This led us to undertake an ab initio analysis of its clusters.

Possibly, the intermolecular interactions between two dimethyl ether molecules are weak relative to those between molecules bearing other oxygen-containing groups. Also, the electrostatic interaction in this molecule probably plays a minor role, so the contribution of the dispersion energy may be more significant than in other cases. As shown in this article, this essentially dispersive nature of dimethyl ether dimer results in differences in its intermolecular behaviour relative to other clusters. One important question to be answered in this respect is to what extent the ether functional group can form hydrogen bonds (viz. intermolecular bonds between a hydrogen atom and an oxygen atom) and, if it does, what geometric and energy properties does it possess.

Apart from these considerations, dimethyl ether is important because ethers are widely used as nonprotic solvents in organic syntheses; however, because of its low boiling point, dimethyl ether is not among the most frequently used solvents for this purpose. In any case, it is the simplest ether and can thus be used to characterize intermolecular interactions in these types of solvents.

The interactions between dimethyl ether and various cations have been modelled on the basis of a number of experimental [5–7] and theoretical studies [8–11], as well as on liquid-phase simulations [12–16]. The primary interest in these systems lies in the extremely valuable ability of ethers to solvate alkaline cations while leaving the corresponding counterions relatively free to react in the medium. Dimethyl ether has also been used as the precursor in developing a model for poly(ethylene oxide), which is a typical substance in some polymers.

The significance of the previously mentioned properties of ethers, in general, and dimethyl ether, in particular, has promoted the development of intermolecular potentials [17–19] to simulate the liquid phase of dimethyl ether substance. All these potentials are empirical in nature – no ab initio potential appears to have been reported so far. In practical terms, a theoretical study of dimethyl ether dimer could be used as the starting point for the development of an ab initio potential and also as a reference to validate empirical potentials.

This study analyses the different lowest-energy conformations for dimethyl ether dimer in the gas phase by using ab initio techniques. The local minima thus identified are characterized in structural, energetic and thermodynamic terms.

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2 Computational details

A number of minima for dimethyl ether dimer were located. To this end, the conformations corresponding to the minima identified by using an empirical potential in previous work [18] were employed as starting geometries (Fig. 1). Additional geometries were chosen on the basis of interactions and geometries present in dimers of other substances (acetone, formaldehyde, acetaldehyde, etc.) containing oxygen atoms and from the results obtained for systems related to dimethyl ether. All degrees of freedom for each conformation studied were optimized by ab initio calculations. The ab initio method used considered electron correlation via Møller–Plesset second-order perturbation theory (MP2). The exploration was carried out at the MP2/6-31 + G** level. The trace of the molecular polarizabilities obtained at this level is 86.5% of the trace obtained by a Sadlej basis set [20], viz. (10s6p4d/6s4p)/[5s3p2d/3s2p], which usually represents these properties quite accurately. In view of this fact, we considered this level of calculation as a reasonable option to deal with the intermolecular interactions in dimethyl ether. It underestimates the dispersion energy by roughly 25–30%. More accurate calculations to characterize the minima found would be too expensive. The minima were characterized from harmonic frequencies and force constants (no negative eigenvalues of the force constant matrix) obtained at the same level. All energies thus obtained, ΔE, were corrected for the basis set superposition error (BSSE) using the counterpoise (CP) method [21]. Thermodynamic properties were determined by using statistical thermodynamic expressions as applied to ideal gases [22]. The dimerization energy was obtained from

$$\Delta U^{\mathrm{T}}_{\mathrm{dim}} = \Delta E_{\mathrm{e}} + \Delta E^{\mathrm{T}}_{\mathrm{vib}} - 3RT \ , \tag{3.1}$$

the enthalpy of dimerization from

$$\Delta H^{\mathrm{T}}_{\mathrm{dim}} = \Delta U^{\mathrm{T}}_{\mathrm{dim}} - RT \tag{3.2}$$

and the Gibbs free energy from

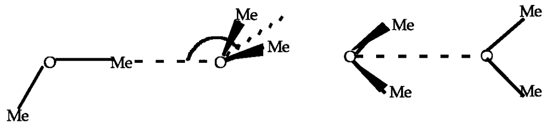
$$\Delta G^{\mathrm{T}}_{\mathrm{dim}} = \Delta H^{\mathrm{T}}_{\mathrm{dim}} - T\Delta S^{\mathrm{T}}_{\mathrm{dim}} \ , \tag{3.3}$$

where $\Delta E^{\mathrm{T}}_{\mathrm{vib}}$ is the vibrational energy change due to dimerization. This term comprises the vibrational energy at point zero and a statistical contribution that reflects the Boltzmann distribution of the vibrational degrees of freedom. Based on a harmonic oscillator approximation, $E^{\mathrm{T}}_{\mathrm{vib}}$ can be expressed as

$$E^{\mathrm{T}}_{\mathrm{vib}} = \frac{1}{2} h \sum_i \nu_i + \sum_i h\nu_i / (\mathrm{e}^{h\nu_i/RT} - 1) \ , \tag{3.4}$$

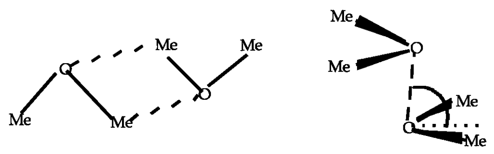
where h is the Planck constant and ν_i denotes vibrational frequencies.

All computations were carried out using the Gaussian 94 statistical software suite [23].



Linear E= -6.57 kJ/mol

Bifurcated E= -9.25 kJ/mol



Cyclic E= -5.73 kJ/mol

Antiparallel E= -7.24 kJ/mol

Fig. 1. Lowest-energy conformations obtained by using an optimized potential for liquid simulations for dimethyl ether dimer

3 Results and discussion

We carried out ab initio explorations of the intermolecular surface of dimethyl ether dimer, which were subsequently used in a deeper study of intermolecular interactions in this system.

To our knowledge, the sole reported data for dimethyl ether dimer appear to be those obtained by Briggs et al. [18] using an empirical potential (viz. an optimized potential for liquid simulations, OPLS). The conformations of the minima predicted by these authors, and their energies, are shown in Fig. 1. As can be seen, the potential is of the heavy-atom type and the whole methyl group is represented by a single interaction centre.

The lowest-energy structures obtained from the ab initio exploration at the MP2/6-31 + G** level are shown in Fig. 2 and their energies are listed in Table 1. A comparison of the ab initio results with those provided by the empirical potential leads to classifying conformation **IV** as "linear". The ab initio calculations predict conformation **IV** as a minimum with low stability [the lowest at the MP2/6-311++G(2d,2p) level]. According to the empirical potential the "linear" conformation is more stable than is suggested by the ab initio results, making this conformation more stable than the "cyclic" conformation. The lowest-energy conformation for the empirical potential is the so-called "bifurcated" conformation. This structure has no clear-cut match in the ab initio results, although it shows some similarity with the secondary minimum denoted by **III** (note that this minimum has both molecules in the same plane). The other two conformations, "cyclic" and "antiparallel", do have ab initio counterparts; however, the stability sequence is the reverse with respect to the optimized minima. These differences between the OPLS and the ab initio calculations are likely to be due to the fact that in the empirical potential the hydrogens are not explicitly defined, resulting in an approximate description of the interactions between these atoms and the oxygens. Another problem with the empirical potential for the description of the dimer minima could be a poor representation of the dispersion and the electrostatic interactions.

Ab initio single-point calculations at the MP2/6-311++G(2d,2p) level were performed for the structures obtained using optimizations at the MP2/6-31 + G** level. The energies obtained (Table 1) are about 1–3 kJ/mol more stable than the MP2/6-31 + G** energies. There is a change in the stability sequence of the energies. Minimum **III** is more stable than minimum **IV** and the same occurs between minima **V** and **II**. These changes are likely to be due to the great importance of the dispersion interactions, which were not sufficiently well described at the MP2/6-31 + G** level. Also note that this new stability sequence is different compared to the one produced by the OPLS.

In addition to the previously mentioned minima, the ab initio calculations suggest the presence of two stationary points that are worth some comment. The points in question are **VI** and **VII** in Fig. 3. As can be seen, these conformations are apparently of preferentially

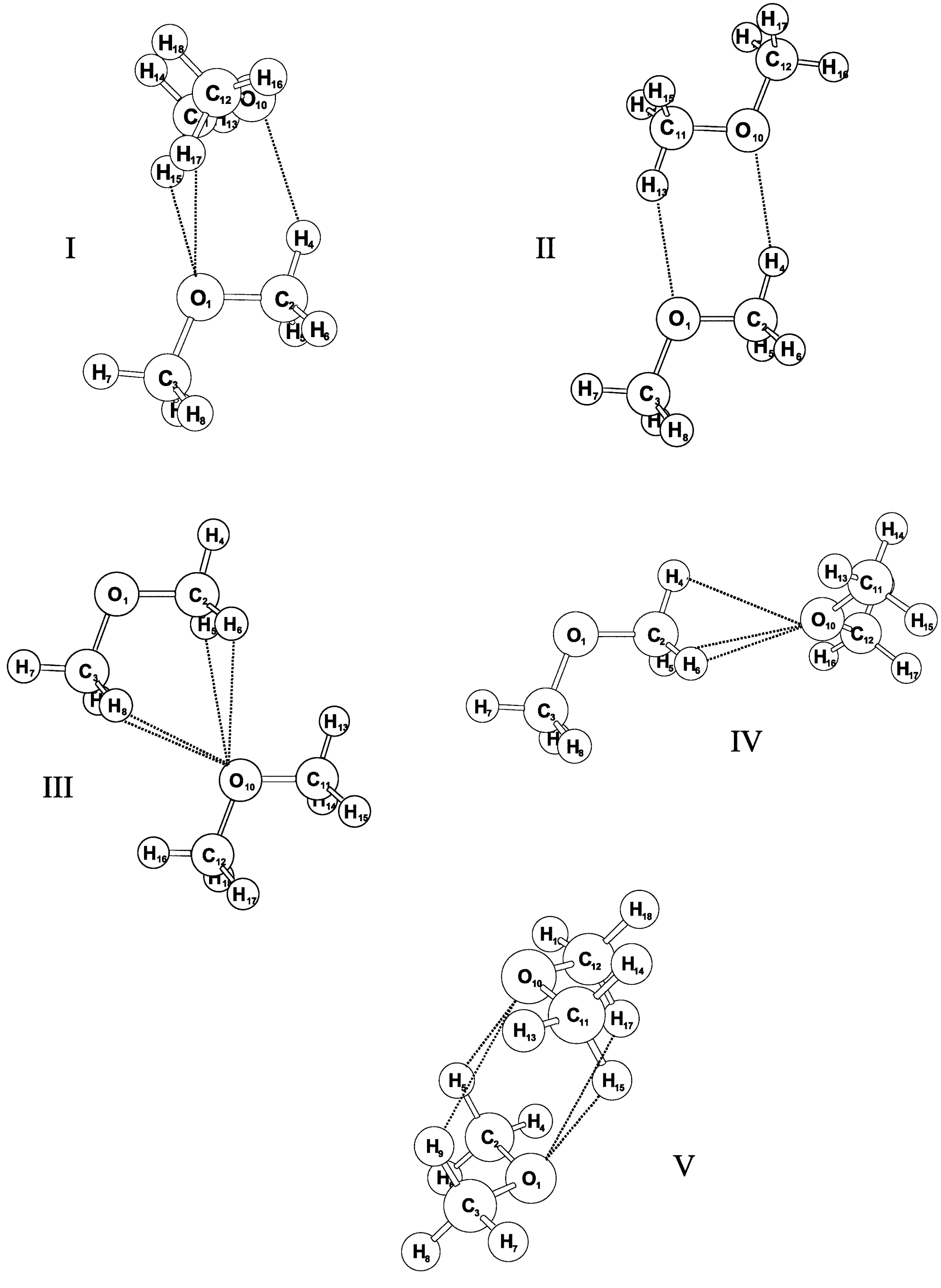


Fig. 2. Structures of the minima identified at the second-order Møller–Plesset/6-31 + G** level

repulsive nature. However, the ab initio exploration reveals that conformation **VI** is a transition state of energy −0.75 kJ/mol and that conformation **VII** a second-order stationary point of energy −0.50 kJ/mol. The calculations predict two positive frequencies below 25 cm^{-1} for the former structure and three for the latter. This

Table 1. Thermodynamic properties (kJ/mol) at 298.15 K of the minima of dimethyl ether dimer as calculated at the second-order Møller–Plesset(*MP2*)/6-31 + G** level

	I	**II**	**III**	**IV**	**V**
ΔE	−9.76	−9.15	−4.17	−4.51	−7.61
	(−11.81)[a]	(−10.12)[a]	(−5.85)[a]	(−5.40)[a]	(−10.95)[a]
D_0	−6.87	−7.10	−2.88	−3.30	−4.12
ΔU_{dim}	−1.96	−1.45	3.09	2.76	0.26
ΔH_{dim}	−4.44	−3.95	0.61	0.26	−2.21
ΔG_{dim}	24.64	20.42	21.98	18.33	28.21

[a] Energies at the MP2/6-311 + + G(2d,2p) level

suggests that the potential-surface regions concerned are very flat.

Minimum **II** exhibits a phenomenon that can be ascribed to BSSE; thus, this conformation exhibits a structure with the molecules in a coplanar arrangement and a very close one where the molecules are not in the same plane. The ab initio absolute energy of the latter structure is more negative than that of the former. It appears as a minimum and the planar one as a transition state; however, after the BSSE CP correction, the interaction energy of the planar configuration is 0.11 kJ/mol more stable than the nonplanar arrangement. Recently, Simon et al. [24] observed the same behaviour in other systems and traced it to BSSE.

Structure **II** is the one which most clearly suggests the presence of hydrogen bonds in this system; this minimum must therefore be of electrostatic origin. This conformation may contain two hydrogen bonds, so the energy of each can be estimated to be about −5.06 kJ/mol at the MP2/6-311 + + G(2d,dp) level. The other minima exhibit no clear signs of the presence of hydrogen bonds. This is in accordance with the fact that the dispersion energy contributes significantly to stabilize these structures, as is shown by the energy differences between the MP2/6-31 + G** and MP2/6-31++G(2d,2p) levels. The increase in the stability is around 30% in minima **III** and **V**, 16% for minima **I** and **IV** and 10% for minima **I**. This importance of the dispersion in minima **III** and **V** is indicated by the Hartree–Fock (HF) computations. On the basis of these, minima **III** and **V** do not exist. In fact they converge to minimum **I**. Minimum **II** is the most stable conformation at this level, even though the energy difference from minimum **I** is only 0.4 kJ/mol.

Assuming that conformation **V** is a result of four "hydrogen bonds" between the oxygens and hydrogens, we obtain an energy at the MP2/6-311 + + G(2d,2p) level of −2.74 kJ/mol for each "hydrogen bond". By analysing conformation **I** as composed of two of these "hydrogens bonds" and one formal hydrogen bond (as appears in conformation **II**), the energy obtained for this conformation would be −10.54 kJ/mol. This is 1.27 KJ/mol higher than the interaction calculated at the MP2/6-311 + + G(2d,2p) level. This shows the subtle balance between electrostatic and dispersion interaction relevant for the formation of the different minima of this molecule, and indicates the difficulties of constructing pair potentials as OPLS, which is based on a general parameterization using different molecules.

The thermodynamic properties at 298.15 K of the ab initio minima at the MP2/6-31 + G** level are summarized in Table 1. As can be seen, the energy D_0 obtained by subtracting the zero-point energy from the electronic energy, ΔE, results in a stability sequence that differs from the original one. Thus, conformation **I** is less stable than **II**; also, the D_0 value for **V** is close to those of the most unstable minima owing to the marked stability loss in this conformation. On the other hand, the sequences for the internal energy, ΔU_{dim}, and enthalpy, ΔH_{dim}, coincide again with the original stability sequence. The sequence, however, is dramatically altered if the entropic factor is included. The Gibbs free energy, ΔG_{dim}, through which the factor is considered, results in a sequence that is rather different from the original situation and where minimum **V** is the most unstable conformation at 298.15 K. The **II**:**I**, **IV**:**I** and **IV**:**II** population ratios are 5:1, 13:1 and 4:1, respectively. Similar results would be obtained using the energies at the MP2/6-311 + + G(2d,2p) level as starting points to calculate the thermodynamic properties, except that a higher stability would be obtained for minimum **V** owing to the bigger change in energy.

The intermolecular coordinates for the stationary points found are given in Table 2. Note that conformation **V** has the shortest intermolecular distance, which is why its energy is also possibly the most strongly influenced by BSSE. As already described, conformer **II** is the one most clearly exhibiting the ability to form hydrogen bonds. This is confirmed by its structural data: its ab initio O···H distances (in the region of 2.4 Å) are shorter than the rest. The next conformer in the distance sequence is **I**, for which $d_{\mathrm{O}\cdots\mathrm{H}}$ is about 2.5 Å. The other minima have much longer distances (e.g. up to about 3 Å for minimum **III**). On the other hand, the intramolecular geometry is essentially similar for all the ab

Table 2. Intermolecular coordinates (Å and degrees) for the dimer conformations

	$r_{\mathrm{O10\text{-}O1}}$	$\alpha_{\mathrm{O10\text{-}O1\text{-}C2}}$	$\varphi_{\mathrm{O10\text{-}O1\text{-}C2\text{-}C3}}$	$\alpha_{\mathrm{C11\text{-}O10\text{-}O1}}$	$\varphi_{\mathrm{C11\text{-}O10\text{-}O1\text{-}C2}}$	$\varphi_{\mathrm{C12\text{-}O10\text{-}C11\text{-}O1}}$
I	3.463	76.1	180.0	76.5	−122.0	69.5
II	3.614	69.8	−179.9	69.8	−179.9	−179.9
III	3.998	55.5	0.7	124.2	−1.5	178.3
IV	4.465	5.9	−130.6	112.7	166.4	−173.8
V	3.322	85.1	83.0	85.1	−179.9	82.9
VI	5.858	44.9	0.0	44.9	180.0	0.0
VII	6.516	0.0	180.0[a]	0.0	178.3[b]	–

[a] C_{12}-O_1-C_2-C_3 torsion (see text)

[b] C_{12}-O_{10}-C_{11}-C_2 torsion (see text)

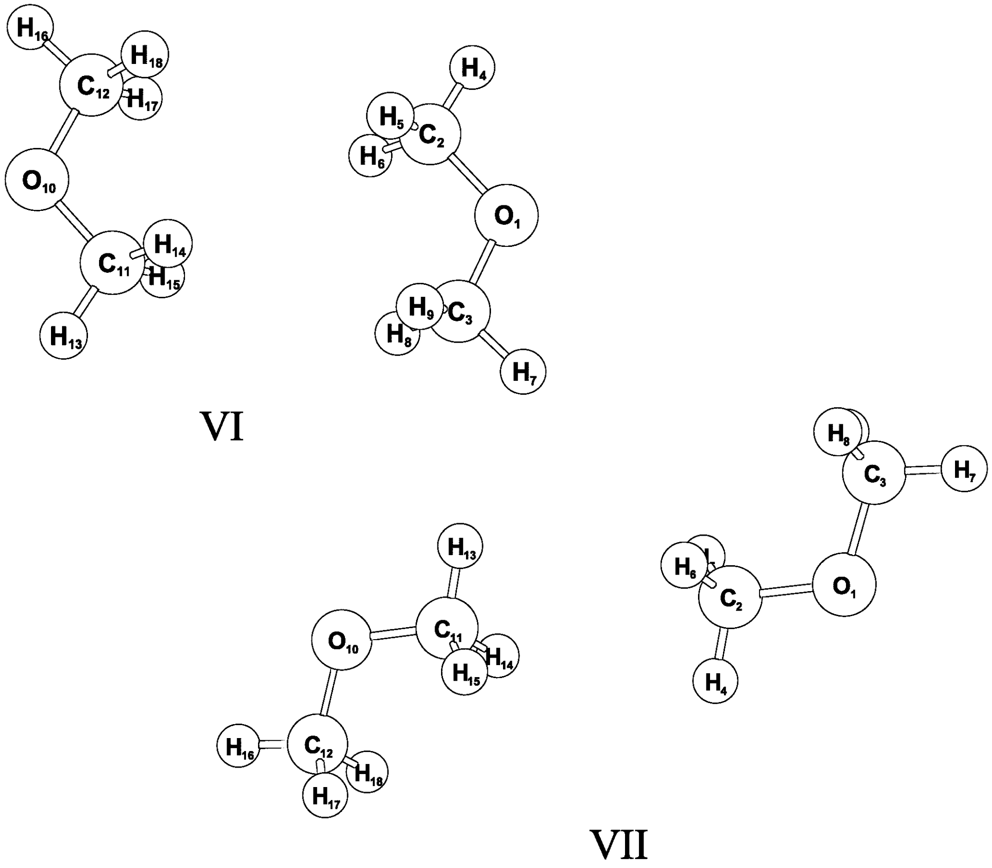


Fig. 3. Conformations of the stationary points

initio optimized dimer conformations; this is reflected in their deformation energy, the highest of which (conformer **II**) is only 0.21 kJ/mol. Finally, it is worth noting that the two ab initio torsions for conformation **VII** shown in Table 2 do not match the labels. The reason is that, as can be seen in Fig. 3, three of the atoms involved in the originally labelled torsions lie in a straight line, so no torsion can obviously be defined. Their substitutes are also shown in Table 2.

4 Conclusions

On the basis of the computations performed, dimethyl ether dimer possesses a highly complex, planar potential surface. The system exhibits five energy minima, only one of which appears to be due to hydrogen bonds [with an energy of −5.06 kJ/mol per bond at the MP2/6-311++G(2d,2p) level]. The other structures are the results of combined interactions of variable nature (hydrogen bonding, van der Waals forces, dispersive forces, etc.).

The energy differences between minima are very small, so much so that inclusion of the entropic factor in addition to the thermal factor dramatically alters the stability sequence.

The contributions of electron correlation yield minima **III** and **V**, which are not obtained at the HF level. A similar situation is observed as regards the two stationary points located, which, on the basis of chemical intuition and their molecular arrangement, could be considered repulsive conformations.

Conformation **II** appears to reflect one of the effects of BSSE. In fact, this configuration exhibits a transition state, the corrected intermolecular energy of which is more negative than that of the minimum itself. This apparent inconsistency is a result of the optimization being performed on a surface not corrected for BSSE. This might also affect the frequencies, changing the nature of structures such as **VI**, with an imaginary frequency of $2i$ cm^{-1}.

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