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Chemical Physics 328 (2006) 251–258

Chemical Physics

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Ab initio calculation of entropy and heat capacity of gas-phase *n*-alkanes with hetero-elements O and S: Ethers/alcohols and sulfides/thiols

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Received 13 April 2006; accepted 5 July 2006
Available online 12 July 2006

Abstract

In this paper, the performance of the one-dimensional hindered rotor approach (1D-HR) is evaluated for *n*-alkanes with hetero-elements O or S. The internal rotations in these molecules show a behavior distinct from those in *n*-alkanes, for which 1D-HR is a cost-efficient method to describe the thermochemical features (entropy and heat capacity). It turns out that also for ethers, alcohols, sulfides and thiols this approach gives a satisfactory experimental agreement. This work confirms earlier results, and consolidates the assumption that the 1D-HR model is highly suitable for reproducing thermodynamic properties of single chain molecules, and that multi-dimensional coupled hindered rotor approaches (*n*D-HR) are not necessarily required for attaining high accuracy. Moreover, it seems that the 1D-HR results are almost independent of the details of the level of theory.

Keywords: Hindered rotor; Entropy; Heat capacity

1. Introduction

The microscopic evaluation of thermodynamic properties of stable species and kinetic data for chemical reactions has now found widespread use in physical chemistry. For molecules containing various single bonds, the one-dimensional hindered rotor (1D-HR) treatment has become an essential tool for an accurate ab initio evaluation of chemical properties. Various works in the literature have shown that the standard harmonic oscillator approach (HO) is inadequate for the treatment of large amplitude vibrations and a correct description of microscopic partition functions and deduced thermochemical and kinetic quantities, and should be corrected with a hindered rotor treatment of the internal rotations. There are different ways to implement the HR concept:

- (i) the simplest corrections can be obtained from the tabulated values proposed by Pitzer in the early days [1],
- (ii) later interpolating formulae between harmonic oscillator (HO) and free rotor (FR) treatments were proposed by Truhlar and co-workers [2],
- (iii) and more recently, a variety of 'full' treatments are proposed by various groups [3–8] in which calculated potentials are used and moments of inertia are calculated from the optimized geometries.

In a previous paper of the authors [7], it was found that the one-dimensional model (1D-HR) was able to reproduce the thermodynamic features – more specifically, third law entropy and heat capacity – of *n*-alkanes quite well (within the level of theory B3LYP/6-311g**).

This hindered rotor study was further elaborated in a more recent paper, where the origin of this good behavior of the 1D model was unravelled [9]. Implementation of the more advanced, coupled 2D-HR method on pentane and the 3D-HR method on hexane, did not result in an improvement

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doi:10.1016/j.chemphys.2006.07.006

of the predictions of entropy, but confirmed the results obtained with the 1D-HR approach. It turned out that the effects of two approximative ingredients inherent to the 1D-HR model – construction of the 1D rotational potential energy and the use of a constant reduced moment of inertia – are systematically cancelled. The conclusions made on *n*-alkanes may not a priori be extended to other single chain molecules.

The goal of this study is a verification whether the excellent performance of the 1D-HR for *n*-alkanes holds for compounds such as ethers and alcohols or sulfides and thiols where a CH_2 fragment is substituted by the hetero-elements O or S. Sufficient experimental data are available to validate the various approximative schemes to handle internal rotors. As already suggested by East and Radom [3] it is not excluded that the standard procedure coinciding with 1D-HR does no longer achieve the desired accuracy for some of these molecules, especially since a conformational study showed that these molecules have a distinct behavior from *n*-alkanes for internal rotations close to the hetero element [10]. We therefore focus on those specific rotations.

The first step in any ab initio study is the selection of an appropriate level of theory. Since there are not always experimental data to benchmark the theoretical data, one has to rely on general studies of similar molecules. This does not give any guaranties. It is therefore important to validate the sensitivity of the HR-corrections to the description of the potential energy. From Ref. [10] one learns that within the B3LYP method, the basis sets 6-31+g* (B1) and 6-311g** (B2) select different geometries as most stable conformer, with only small potential energy differences. Experimental verification suggests that the B1 basis produces the correct results for ethers and alcohols. However, for sulfides and thiols no definite conclusion may be drawn.

Use of the correlation consistent Dunning basis sets (cc-pVDZ and aug-cc-pVDZ) [11] on dipropylether learns that the inclusion of diffuse functions is the crucial ingredient in discriminating between the two types of results on conformational energies obtained by the two basis sets B1 and B2.

We will calculate the entropy and heat capacity of ethers and alcohols with both B3LYP/B1 and B3LYP/B2 levels of theory in the 1D-HR *and* 2D-HR approaches, in order to draw some conclusions about the sensitivity of the HR approach to these differences.

2. Theory

For the evaluation of thermodynamic properties such as entropy and heat capacity directly from the molecular properties, the molecular partition function is needed. In the present case, we use a mixed Harmonic Oscillator/Hindered Rotor model in which all internal motions, except for the internal rotations, are approximated as independent harmonic oscillators, without any additional scaling factors.

The partition function belonging to the internal rotations depends critically upon the way both potential and kinetic energy contributions of the system are calculated.

In the one-dimensional approach (1D-HR) the usual approximation for the potential energy is used: for each internal rotation a one-dimensional potential energy curve (1D-PES) is calculated, and the total multi-dimensional potential energy surface (*m*D-PES) is assumed to be the sum of these one-dimensional contributions:

$$V^{m\mathrm{D}}(\phi_1,\ldots,\phi_m) \approx \sum_{i=1}^{m} V_i^{1\mathrm{D}}(\phi_i). \tag{1}$$

In the 2D-HR method, multiple two-dimensional potential energy surfaces (2D-PES) are constructed and the final potential energy is obtained by subtracting all 1D-PES which are counted twice [12]:

$$V^{m\mathrm{D}}(\phi_1,\ldots,\phi_m) \approx \sum_{i=1}^{m-1} V_{i(i+1)}^{2\mathrm{D}}(\phi_i,\phi_{i+1}) - \sum_{i=2}^{m-1} V_i^{1\mathrm{D}}(\phi_i). \tag{2}$$

The calculation of the moments of inertia is also performed according to well-established methods described in previous papers of the authors [6,7,9,12]: fixed reduced moments of inertia for each single internal rotation for the 1D-HR scheme, in contrast to variable moments of inertia of both global and internal rotations for the 2D-HR model. The calculation of the kinetic energy matrix $A(\phi_1,\ldots,\phi_m)$ is needed for the latter method [13,9,14].

3. Labelling convention for conformers

In order to unambiguously describe the different (reference) conformers, a consistent labelling system must be introduced. This was already done in a previous study on alcohols, thiols, ethers and sulfides [10], and a short overview is outlined in this paragraph.

Individual conformations about an internal rotation are defined as *t*, *g*− and *g*+, corresponding to a *trans* or a *gauche* ∓ orientation. When multiple internal rotations within a molecule are considered, the individual conformation of each rotation has to be assigned. The appropriate labelling convention for a sequence of internal rotations is illustrated in Fig. 1. For alcohols and thiols (Fig. 1a), the first internal rotation (with dihedral angle ϕ_{l1}) is about the CX bond (X = O or S). The other rotations are labelled as ϕ_{lx} where *x* indicates the position of the CC rotation axis in reference to the CX bond. Also the position of the hydroxyl top is written explicitly. For example, the HO*g*+*tg*−*t*

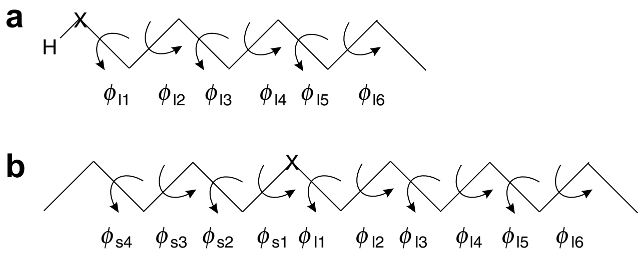

Fig. 1. Labels used to identify specific internal rotations (with their dihedral angles) in: (a) primary alcohols (X = O) and thiols (X = S) and (b) in ethers (X = O) and sulfides (X = S).

conformer of 1-pentanol (or HSg+$tg-t$ for 1-pentane thiol) stands for $\phi_{l1} = g+$, $\phi_{l2} = t$, $\phi_{l3} = g-$, and $\phi_{l4} = g-$, where l4 indicates the ethyl torsion, l3 the propyl torsion, etc.

For ethers and sulfides, the same convention applies, but one has to distinguish between the two alkyl fragments (Fig. 1b). The 'l' subscript indicates that the rotation is situated in the longest alkyl top on the hetero-element, and the 's' refers to the shortest alkyl branch. We refer to a conformer by specifying the individual conformations in the order $\phi_{s\,\max} \ldots \phi_{s1} X \phi_{l1} \ldots \phi_{l\,\max}$, with X = O or S. For example, in ethyl propyl ether tO$g-g+$ stands for $\phi_{s1} = t$, $\phi_{l1} = g-$, and $\phi_{l2} = g+$, while the same configuration in ethyl propyl sulfide is referred to as tS$g-g+$.

4. Potential energy profiles

Because the hetero compounds under study in this work exhibit several (very) low energy conformers [10], one could expect multi-dimensional potential energy surfaces to be different than those obtained in pure n-alkanes [9,12]. We calculate some two-dimensional energy surfaces (2D-PES) that can serve as examples for a whole series of compounds. For *alcohols and thiols*, 1-hexanol and 1-hexanethiol are selected, and all 2D-surfaces are calculated. These plots are displayed in Fig. 2. While the –OH and –*SH* rotations exhibit a very specific behavior, the other surfaces are only slightly different than corresponding plots in n-alkanes. Note that for increasing ϕ_{lx} the $g-g+$ double minimum becomes more pronounced. Less subtle differences are found in *ethers and sulfides*, for which we studied the $\phi_{s1}\phi_{l1}$ and $\phi_{l1}\phi_{l2}$ surfaces, illustrated in methyl propyl ether (MPE) and sulfide (MPS), di-ethyl ether (DEE) and sulfide (DES), and finally di-propyl ether (DPE) and sulfide (DPS).

The $\phi_{l1}\phi_{l2}$ potential energy surfaces (in MPE, DPE, MPS and DPS: Fig. 3) show, compared to a typical n-alkane 2D-PES, mainly one deviating coupling effect: in ethers the typical alkane double minima around the $g-g+$ geometry is completely destroyed (compare with *e.g.* the $\phi_{l4}\phi_{l5}$ surfaces of hexanol and hexanethiol). The $\phi_{s1}\phi_{l1}$ potential energy surfaces (Fig. 4) are very instructive, and show very distinct features for ethers and sulfides. Not only is the behavior around the $g-g+$ geometry different (again), but there are also more minima on the sulfide surfaces. These numerous minima are connected by broad, low energy valleys. Even the energy barriers are substantially lower than in ethers (note the different scale of the contour plots in Fig. 4). The influence of the level of theory on the 2D-profiles is not very pronounced. We display the 2D-PES obtained with the two basis sets B1 and B2 and we scarcely notice any discrepancy on the qualitative level. Still, both levels of theory exhibit a different global minimum, which will result in different one-dimensional paths to be used in the 1D-HR approach.

In particular, the largest deviations are noticed in DPE and to illustrate the variations of the potential energy surface we give the various conformational energies of DPE for the two basis sets B1 and B2 in Table 1. We also include the predictions for two correlation consistent Dunning basis sets [11]. The similarity between the values obtained within the two basis sets involving diffuse functions [6-31+g* (B1) and aug-cc-pVDZ] is striking, and we may conclude that the deviations noticed between the B1 and B2 results are directly linked to the presence or not of diffuse functions in the basis set under consideration. The one-dimensional cuts starting from the global minimum conformation will clearly be different in the two types of bases, giving rise to a completely different 1D-HR description, and causing strongly deviating results.

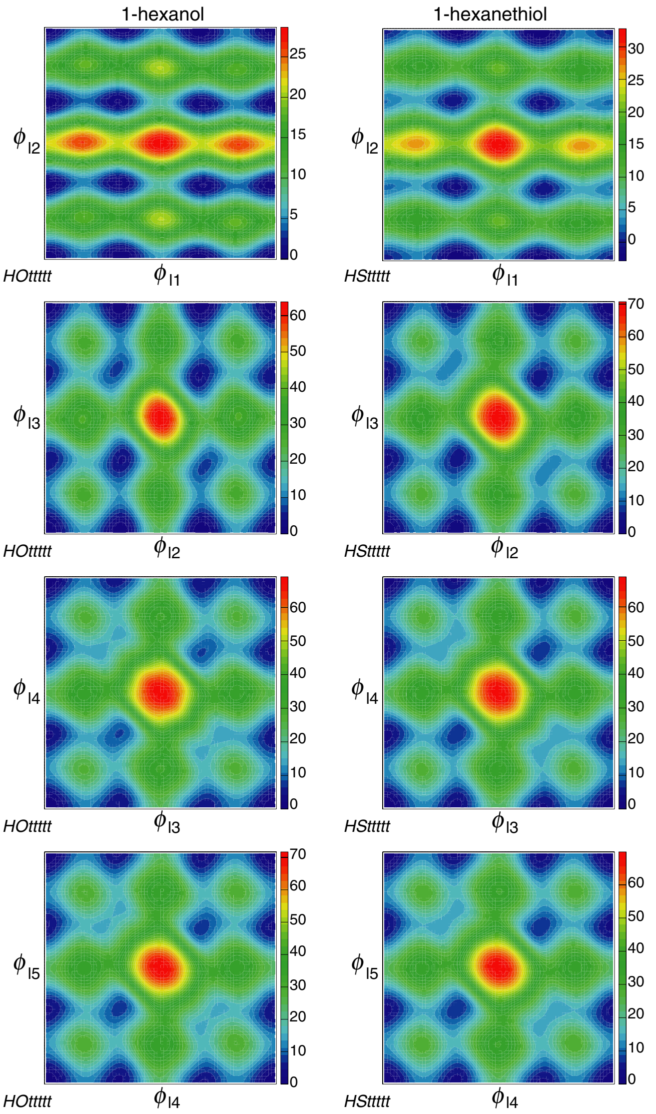

Fig. 2. Two-dimensional potential energy profiles of 1-hexanol (B3LYP/B1) and 1-hexane thiol (B3LYP/B2). The dihedral variation is relative to the all-*trans* conformer: HO*tttt* and HS*tttt*.

Both in 1D-HR and 2D-HR, the methyl top rotations are described one-dimensionally. Their energy profiles are determined unambiguously by the barrier height. For n-alkanes this barrier converges about the value of 12.1 kJ/mol for long enough chains [7]. In n-alkanes with substitution of a CH_2 fragment by an hetero element O or S, the methyl barrier height depends on the position of the hetero

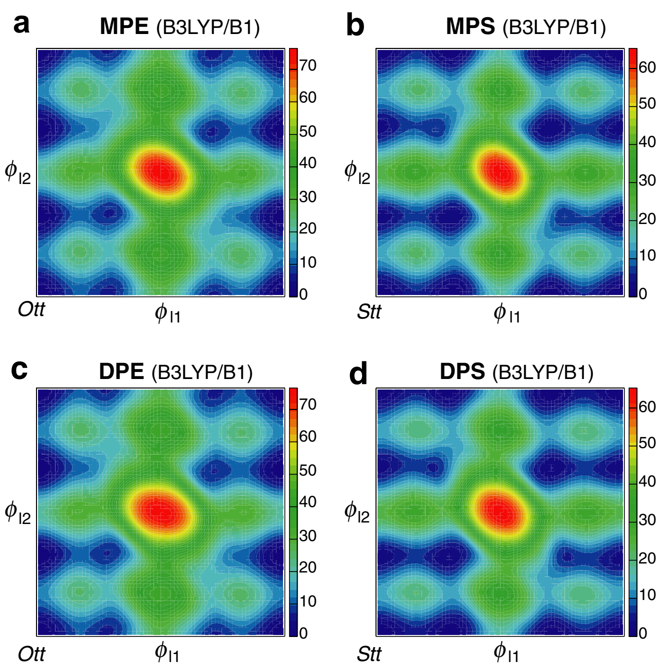

Fig. 3. Two-dimensional potential energy profiles (relative to the all-*trans* conformer: O*tt* and S*tt*) of the $\phi_{l1}\phi_{l2}$ energy surfaces in: (a) methyl propyl ether (MPE), (b) methyl propyl sulfide (MPS), (c) di-propyl ether (DPE) and (d) di-propyl sulfide (DPS) on the B3LYP/B1 level of theory.

element in the chain with respect to the ending methyl top. The largest variations take place in the smallest molecules: C_2H_6O may represent ethanol as well as dimethyl ether (DME) but the barrier varies from 11 kJ/mol (in DME) to 15.5 kJ/mol (ethanol) (Fig. 5). The variation of the barriers decreases for longer hetero substituted alkanes and converges to the pure *n*-alkane value of 12.1 kJ/mol. The lowest barrier is noticed in molecules, where the methyl top is nearest to the hetero element and its magnitude largely depends on the nature of the hetero element: 6 kJ/mol for methyl tops close to S, which may be the result of the (very) long bond length of S–C.

The methyl barrier heights are almost independent of the choice of basis, with differences less than 0.2 kJ/mol.

5. Thermodynamic properties

5.1. Oxygen compounds

Table 2 gives a summary of the results obtained in the considered set of alcohols and ethers[1]. The entropy and heat capacity values are calculated at different levels of theory: B3LYP/6-31+g*(B1) and B3LYP/6-311g**(B2), and also with different calculation schemes: the harmonic oscillator model (HO), and the two hindered rotor schemes 1D-HR and 2D-HR. For transparency, we also report the results from the works from Guthrie [16] and Chen [17] when available. The reference values are taken from Ref. [15].

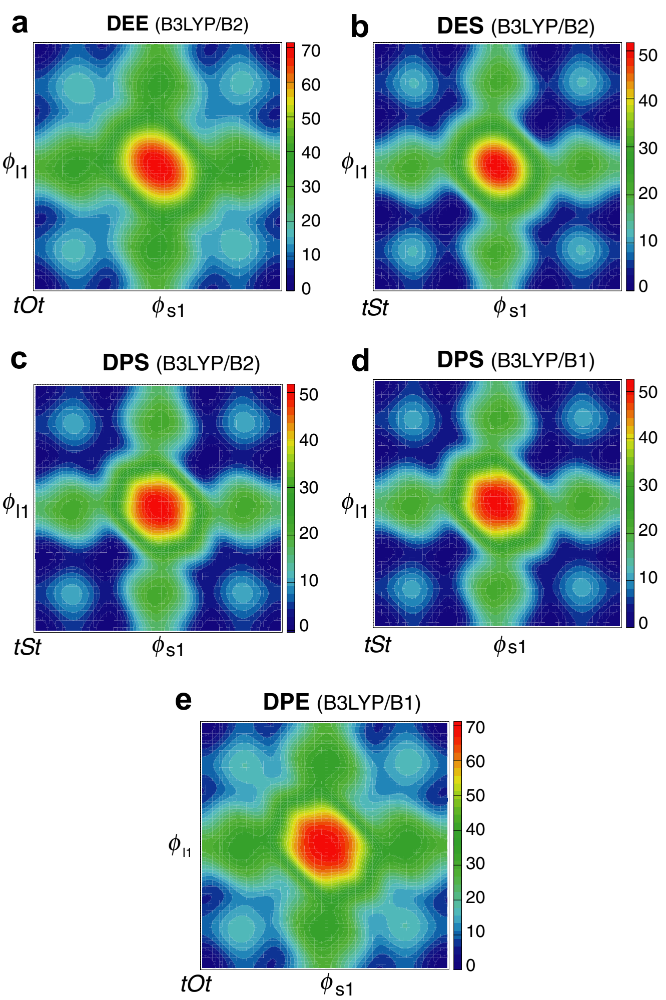

Fig. 4. Two-dimensional potential energy profiles of the $\phi_{s1}\phi_{l1}$ energy surfaces in di-ethyl ether (DEE), di-propyl ether (DPE) and di-ethyl sulfide (DES), di-propyl sulfide (DPS): (a) DEE on the B3LYP/B2 level of theory, (b) DES on the B3LYP/B2 level of theory, (c) DPS on the B3LYP/B2 level of theory, (d) DPS on the B3LYP/B1 level of theory and (e) DPE on the B3LYP/6-31+g*(B1) level of theory.

Table 1
Influence of the basis set on the relative energy of some conformers of di-propyl ether, and on the entropy and heat capacity calculated in the HO approximation

kJ/mol	6-31+g(d) (B1)	6-311g(d, p) (B2)	cc-pVDZ	aug-cc-pVDZ
*tt*O*tt*	0.00	2.51	3.36	0.24
*tt*O*tg*	0.22	1.28	1.66	0.11
*tt*O*gt*	6.24	8.60	8.69	6.24
*tg*O*gt*	11.69	13.36	12.93	11.99
*gt*O*tg*	0.54	0.00	0.00	0.00
J/mol K	6-31+g(d) (B1)	6-311g(d, p) (B2)	cc-pVDZ	aug-cc-pVDZ
S	394.03	388.58	389.17	392.06
C	144.38	143.96	144.46	145.29

The entropy values are given at 298.15 K. All HO predictions systematically underestimate the experimental data. The discrepancies are of the order of 10% of the total magnitude. The full ab initio corrections arising from taking into account 1D internal rotors bring the theoretical

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[1] Supplementary material can be found, online on ScienceDirect at doi:10.1016/j.chemphys.2006.07.006 (http://www.sciencedirect.com).

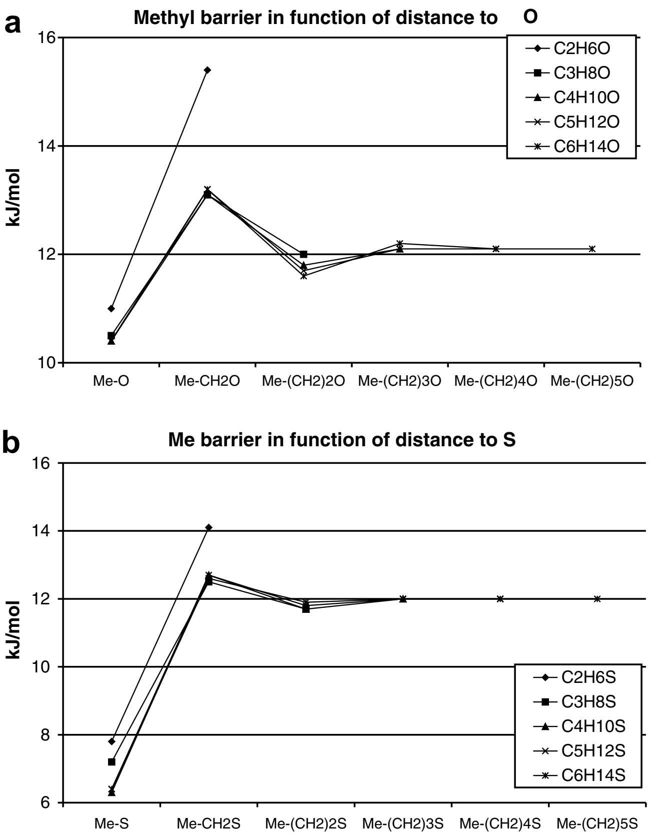

Fig. 5. Methyl top barrier height in function of chain length and position of the hetero element in the chain, calculated at the B3LYP/B2 level of theory. Note that for *n*-alkanes the barrier amounts to about 12.1 kJ/mol.

predictions to values which are very close to the experimental estimates (within a few J/mol K) independent of the level of theory B1 or B2. In some ethers, the agreement is even spectacular, especially on the B3LYP/6-311g**(B2) level of theory. The 2D-HR entropy values are somewhat higher than the 1D-HR results, and the discrepancy with the experimental values increases.

This excellent quality of the 1D-HR results was also noted for *n*-alkanes [7]. Further research revealed that, for those molecules, a cancellation of errors (potential versus kinetic energy) in the construction of 1D-HR partition function [9] lies at the origin of its success.

For some selected molecules the 2D-HR procedure has also been applied. It turns out that the agreement with experiment is not improving. In most of the cases, the 2D-HR model overestimates the entropy. To illustrate with an example: in dipropyl ether (DPE) the 2D-HR correction with respect to the HO estimate amounts to 40.5 J/mol K, compared to 35.7 J/mol K in the 1D-HR model. They both overestimate the experimental value with, respectively, 12.1 and 7.2 J/mol K. This result is rather surprising as it does not happen frequently that a more elaborated method turns out to be less adequate than the more simplified one. It is probably due to some hazardous cancellation of errors as already emphasized in previous works (Refs. [9,14]). In addition the calculated value of the entropy for dipropyl ether strongly depends on the basis set chosen

Table 2
Entropy and heat capacity of alcohols and ethers at 298.15 K

	Basis	S (298.15 K)	C (298.15 K)
Ethanol			
Ref. values [15]		282.59	66.17
HO	B1	269.68	64.65
	B2	268.78	64.63
1D-HR	B1	278.11	64.88
	B2	282.33	65.38
Dimethyl ether			
Ref. values [15]		266.69	66.03
HO	B1	264.47	62.43
	B2	264.48	62.68
1D-HR	B1	267.28	65.04
	B2	269.15	65.26
1-Propanol			
Ref. values [15]		324.72	93,48
HO	B1	301.81	85.03
	B2	298.93	84.47
1D-HR	B1	324.25	86.60
	B2	322.05	86.84
Methyl ethyl ether			
Ref. values [15]		310.62	92.04
HO	B1	302.05	82.99
	B2	302.26	83.32
1D-HR	B1	309.88	92.94
	B2	311.89	92.77
Chen [17]		312.63	92.47
1-Butanol			
Ref. values [15]		362.75	111.91
HO	B1	333.82	105.22
	B2	331.28	104.78
1D-HR	B1	365.44	112.09
	B2	362.36	111.56
Guthrie [16]		361.00	
Methyl propyl ether			
Ref. values [15]		349.13	112.38
HO	B1	334.60	103.34
	B2	332.56	103.29
1D-HR	B1	351.13	114.22
	B2	349.71	112.75
2D-HR	B1	352.71	114.12
Guthrie [16]		352.21	
Diethyl ether			
Ref. values [15]		341.00	118.26
HO	B1	327.74	103.53
	B2	328.56	103.99
1D-HR	B1	341.96	120.64
	B2	341.61	119.80
2D-HR	B2	347.90	119.66
Guthrie [16]		345.97	
1-Pentanol			
Ref. values [15]		402.50	133.70
HO	B1	364.55	125.32
	B2	362.57	125.10
1D-HR	B1	408.39	137.48
	B2	402.81	136.21
Guthrie [16]		401.45	
Methyl butyl ether			
Ref. values [15]		390.10	
HO	B1	366.80	123.57
	B2	364.74	123.70

(*continued on next page*)

Table 2 (*continued*)

	Basis	S (298.15 K)	C (298.15 K)
1D-HR	B1	389.05	139.87
	B2	389.46	138.61
Ethyl propyl ether			
Ref. values [15]		388.10	134.49
HO	B1	366.56	123.94
	B2	365.01	123.99
1D-HR	B1	384.83	141.82
	B2	386.91	139.85
1-Hexanol			
Ref. values [15]		441.50	156.97
HO	B1	398.31	145.84
	B2	395.26	145.57
1D-HR	B1	442.06	163.17
	B2	445.57	161.02
2D-HR	B1	446.32	161.97
Guthrie [16]		441.83	
Methyl pentyl ether			
Ref. values [15]			
HO	B1	398.95	143.89
	B2	397.28	144.11
1D-HR	B1	421.17	165.18
	B2	417.12	163.74
Ethyl butyl ether			
Ref. values [15]		429.00	157.75
HO	B1	398.70	144.12
	B2	396.45	144.32
1D-HR	B1	424.12	167.46
	B2	427.72	165.93
Dipropyl ether			
Ref. values [15]		422.50	153.41
HO	B1	394.03	144.38
	B2	388.58	143.96
1D-HR	B1	429.74	163.08
	B2	420.92	160.23
2D-HR	B1	434.57	163.49
Guthrie [16]		428.53	

and can differ substantially (approximately 9 J/mol K). It has already been observed that the presence of diffuse functions in the basis set lies on the origin of these discrepancies. This is confirmed by the estimates made in the more advanced cc-pVDZ and aug-cc-pVDZ basis sets (see Table 1) within the full HO approximation. The two basis sets B1 and B2 predict HO estimates differing by 5.5 J/mol K (calculated with respect to the reference conformers *tt*O*tt* and *gt*O*tg*, respectively). This suggests that the vibrational modes strongly depend on the structure, and assuming their harmonic description fixed for other geometries than the reference conformer may generate large errors. In a recent paper, we have shown that even minor changes in the vibrational modes can lead to different predictions of thermodynamic quantities [14]. In this work, a more elaborated 'extended hindered rotor' (EHR) model has been developed and could be regarded as the 'exact' reference model instead of the 2D-HR approach. However, EHR needs the calculation of the complete *m*D-PES, and is therefore not the most appropriate method for *e.g.* dipropyl ether ($n = 4$).

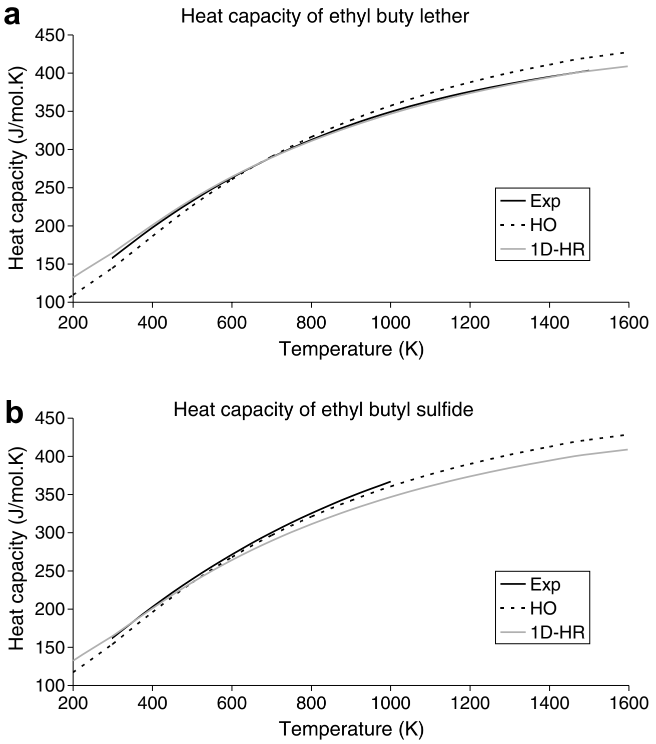

Fig. 6. Heat capacity in J/(mol.K) of: (a) ethyl butyl ether and (b) ethyl butyl sulfide.

The reproduction of the heat capacity is of the same order of accuracy as observed in *n*-alkanes, and almost independent of the specific HR scheme (1D or 2D). The calculated values are somewhat too high for lower temperatures as a result of the classical implementation of our hindered rotor treatments [7]. On the other hand for medium and higher temperatures we achieve a very satisfactory agreement. In Fig. 6a, the temperature behavior of the heat capacity in ethyl butyl ether is plotted. It confirms our conclusions.

5.2. Sulfur compounds

Entropy and heat capacity values for the selected set of thiols and sulfides are presented in Table 3[2]. The reference values are taken from Ref. [15]. When available, the results of Guthrie's work [16] are also reported.

The agreement of the calculated entropy values with experiment is satisfactory but not of the same level as for alcohols and ethers. While the HO results still underestimate the experimental values significantly, the 1D-HR predictions are close to experiment, except for some smaller sulfides. For dimethyl sulfide, methyl ethyl sulfide and diethyl sulfide the HO values are already reproducing the entropy quite well, and the 1D-HR and 2D-HR predictions now exceed the experimental data. Both models predict

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[2] Supplementary material can be found online on ScienceDirect at doi:10.1016/j.chemphys.2006.07.006 (http://www.sciencedirect.com).

almost the same entropy values, the differences are small compared with the corrections obtained in alcohols and ethers. Anyway, as before, the best overall agreement is given by the 1D-HR approach.

The analysis of the heat capacities reveals some interesting features. For higher temperatures, the HO approximation will normally provide an upper limit for the heat capacities, as the contribution for each activated mode will be R, while for the HR modes it will tend to $R/2$. This rule indicates that the HO models are expected to overestimate the heat capacity at high temperatures. This rule is not systematically respected in Table 3. For the larger molecules (such as 1-butanethiol) the experimental heat capacities are larger than those predicted in the HO approximation!

As the HR model lowers the heat capacity values by $R/2$ (at high temperatures) for each internal rotation present, the 1D and 2D-HR predictions will be worse than the HO values. This situation is shown in Fig. 6b. This failure in reproducing the correct behavior of the heat capacity in sulfides lies in the presence of low vibrational modes. Contrary to ethers and n-alkanes, there are low temperature bending modes resulting from the heavy S atom and the long CS bonds. They are responsible for higher moments of inertia ($I \sim r^2 = |\mathrm{CS}|^2$) and hence lower HO frequencies ($\sim (\frac{V''}{I})^{1/2}$; with V'' the second-order derivative of the potential energy along the bending mode). As the vibrational temperatures originating from these bending modes are of the same magnitude of the vibrational temperatures of internal rotations, they are heavily mixed. This is confirmed by visual inspection of the normal modes.

Low and medium vibrational modes contribute strongly to the heat capacity value. Therefore, their frequency should be determined very accurately. This requires a high level of theory.

6. Summary

In this work the thermodynamic properties – entropy and heat capacity – of alcohols/thiols and ethers/sulfides have been the subject of a thorough investigation. In these molecules, several internal rotations are present. These rotations have a tendency to generate multiple conformers with similar energies, and may exhibit, depending on the level of theory, a global potential energy minimum at a conformation different from the all-*trans* geometry. Both properties are different from n-alkanes in which there is a distinct energy minimum at the all-*trans* conformation. It was therefore difficult to predict if the 1D-HR approach would be able to reproduce the experimental data on entropy and heat capacity with the same kind of accuracy as for n-alkanes.

The 1D-HR method is indeed capable of reproducing entropy values close to experiment. The 2D-HR method, although theoretically more evolved, seems to slightly overestimate the entropy.

The prediction of the heat capacity on the other hand is more problematic: the reproduction of heat capacities in

Table 3
Entropy and heat capacity of thiols and sulfides at 298.15 K

	Basis	S (298.15 K)	C (298.15 K)
Ethanethiol			
Ref. values [15]		296.02	74.37
HO	B2	284.63	70.94
1D-HR	B2	293.45	72.54
Dimethyl sulfide			
Ref. values [15]		285.85	75.22
HO	B2	284.56	72.18
1D-HR	B2	292.79	73.18
1-Propanethiol			
Ref. values [15]		336.50	96.86
HO	B2	317.39	91.63
1D-HR	B2	335.34	95.92
Methyl ethyl sulfide			
Ref. values [15]		333.15	95.04
HO	B2	323.62	92.44
1D-HR	B2	341.42	93.91
1-Butanethiol			
Ref. values [15]		375.20	120.58
HO	B2	348.69	111.84
1D-HR	B2	373.17	120.79
Methyl propyl sulfide			
Ref. values [15]		371.68	117.29
HO	B1	355.85	112.15
	B2	353.75	113.10
1D-HR	B1	375.44	117.21
	B2	374.91	117.76
2D-HR	B1	376.67	117.09
	B2	376.21	116.84
Diethyl sulfide			
Ref. values [15]		368.00	120.11
HO	B2	351.59	112.75
1D-HR	B2	378.55	114.49
2D-HR	B2	378.29	114.56
1-Pentanethiol			
Ref. values [15]		415.39	141.78
HO	B2	380.35	132.16
1D-HR	B2	417.48	146.06
Methyl butyl sulfide			
Ref. values [15]		411.90	140.67
HO	B2	385.95	133.43
1D-HR	B2	414.98	142.99
Guthrie [16]		414.47	
Ethyl propyl sulfide			
Ref. values [15]		414.12	139.02
HO	B2	387.43	133.34
1D-HR	B2	415.95	139.00
Guthrie [16]		405.76	
1-Hexanethiol			
Ref. values [15]		454.70	167.69
HO	B2	411.60	152.51
1D-HR	B2	457.18	170.88
2D-HR	B2	460.64	168.85
Guthrie [16]		457.73	
Methyl pentyl sulfide			
Ref. values [15]		451.18	163.50
HO	B2	418.80	153.85
1D-HR	B2	450.18	168.29
Guthrie [16]		453.67	

(*continued on next page*)

Table 3 (*continued*)

	Basis	S (298.15 K)	C (298.15 K)
Ethyl butyl sulfide			
Ref. values [15]		453.39	161.85
HO	B2	418.56	153.62
1D-HR	B2	453.89	164.11
Dipropyl sulfide			
Ref. values [15]		448.80	161.10
HO	B1	417.17	152.75
	B2	412.56	154.06
1D-HR	B1	444.99	161.25
	B2	451.89	162.75
2D-HR	B1	452.33	160.49
	B2	449.76	160.59
Guthrie [16]		450.91	

alcohols and ethers is satisfactory, but the hindered rotor *and* harmonic oscillator models fail to predict reliable values in thiols and sulfides.

The general conclusion is that the 1D-HR approach is a very satisfactory model to describe the entropy of the presented single chain molecules: primary alcohols and thiols, and ethers and sulfides. The calculated values are rather insensitive to the details of the description: both B3LYP/6-31+g* and B3LYP/6-311g** perform very well, although the basis set B3LYP/6-31+g* including diffuse functions (and in analogy the basis set aug-cc-pVDZ) should be the appropriate level of theory to describe the energy differences between the conformers.

This is a very useful property of 1D-HR, since the time-consuming step of the level of theory study can be reduced considerably.

Acknowledgements

This work is supported by the Fund for Scientific Research – Flanders (FWO) and the Research Board of Ghent University.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chemphys.2006.07.006.

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