Molecular Electronic Structure 2014 (MES 2014) Symposium



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The Molecular Electronic Symposium - MES 2014 was held in Amasya (Turkey) between 01-05 September, 2014. The next MESBA 2016 will be in Buenos Aires, 19-23 September.

The previous (inaugural) MES symposium was organized in Çanakkale, Turkey (2012).

MES symposiums propose to bring theoreticians together peacefully to present recent progress in explicit electron correlation, molecular integration over exponentially decaying orbitals, extrapolation methods and novel methods in quantum physics for molecules and solids.

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Preface

These proceedings collect some of the work presented at the Molecular Electronic Symposium - MES 2014. It contains applications of quantum chemistry methods at the (Density Functional Theory) DFT level to a some 'real' systems, of interest to chemistry and cross-disciplinary fields.

The neurotransmitter cyclodextrin, cadmium telluride and its zinc alloy, enantioselective catalytic synthesis and mild oxidation in metal oxide catalysts.

Hopefully, you will enjoy reading them as much as we enjoyed compiling this volume.

P.E. Hoggan Clermont, 25.4.2016.

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A quantitative relationship between the energy of complexation of neurotransmitters: β-cyclodextrin complexes and their different properties

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Abstract: This research work deals with the complexation to β -cyclodextrin (CD) of the neurotransmitter molecules (catecholamines DA, NA and A, serotonin (S), and ascorbic acid, AA) w using the ONIOM method. Two critical levels are considered. First, density functional theory is used with B3LYP functional and the 6-31G* level that is performed on the guest molecule. Second, the Hartree-Fock method is used with 3-21G* basis set for the β -CD.

The QSPR approach was used to establish a quantitative relationship between the complex energies and the electronic, the steric, and the hydrophobic properties of the guest molecules to determine the factors affecting the complexes stability. These factors are fixed by MLR and PLS models mainly corresponding to E_{HOMO} , E_{LUMO} (eV), Log P_{Marvin}, μ (D), Gap E_{HOMO} - E_{LUMO} of the guest and VDW, and Gap E_{HOMO} - E_{LUMO} of the complex.

The proposed model has an improvement equal to 3.20%, when it was applied to the validation set. As long as the average cross validation error is below 11.5%, an excellent prediction capability was observed.

Introduction

Recently the quantum chemistry world has turned its interest to the development of the so called hybrid techniques that make use of different methods to deal with different parts of the system [1]. The idea behind these methods is that chemical reactions in large systems directly involve only a small number of atoms so that these atoms are treated by a sophisticated and accurate method. The rest of the system can be satisfactorily dealt with by a less accurate and computationally cheaper method. Among these hybrid methods the ONIOM (Our Own N-layered Integrated Molecular Orbital Mechanics) method developed by the Morokuma group, is especially appealing as it can combine virtually any quantum chemistry or molecular mechanics method with each other [2].

The ONIOM method has dramatically extended the scale of chemical and biological systems which can be investigated by the extensive quantum chemical arsenal available today [3-9]. Such an approach is very useful in systems of supra-molecular chemistry such as the inclusion complexes [10-14].

In our research, the ONIOM method is used in order to obtain the real geometry and for providing further insight into the complexation process for each of the neurotransmitter molecules (catecholamines DA, NA and A, serotonin (S), and ascorbic acid, AA) with β -CD. In this research work only two levels of the ONIOM procedure are used, they are defined as the following:

(i) Density functional theory with B3LYP functional where the 6-31G* basis set was performed on the guest molecule.

(ii) Hartree-Fock method with the 3-21G* basis set was used for the β -CD.

The inclusion complexes are characterized by non-covalent interactions that require a combination of several theoretical methods to determine the factors affecting their energy. The new modeling techniques involving the relationship between structure and biological activity [15, 16] has become an attractive, and valuable approach, especially in cases where the availability of samples is limited, or experimental measurements are dangerous, time consuming and expensive.

Quantitative Structure Property Relationship QSPR studies are powerful methods to design the bioactive compounds and the prediction of activity according to the physical and chemical properties [17-19].

The objective of QSPR modeling is to find an accurate, robust and applicable model that can be used in understanding how chemical structure relates to the biological activity of natural and synthetic chemicals in addition to the designation of newer and better therapeutics. These models are a statistical solution to the problem of directly calculating physical and biological properties of molecules depending on their structures [20].

This research area aims to correlate molecular structures represented by the coded numeric descriptor, with their properties using computer modeling techniques and mathematics.

The QSPR models obtained must possess appropriate characteristics, namely: precision, accuracy, stability and prediction.

Selecting the descriptor information included in each model is a difficult task. On one hand, it is difficult to select that of each model.On the other hand, it is very relevant because it allows us to determine the physicochemical parameters that have major influence on the activity and thus allows us to design new structures to improve the biological effect sought.

To achieve this goal, we planned to generate QSPR models for a set of inclusion complexes of neurotransmitter molecules. Each of the (catecholamines DA, NA and A, serotonin (S)) Fig.1, and ascorbic acid, AA Fig.2) with β -cyclodextrin that is presented in Scheme 1 in which the QSPR models related to the energy of complexation with different electronic and structural properties is plotted. According to the jargon of supramolecular chemistry these properties are known as the "driving forces".

Methodology

DFT and ONIOM2 calculations were carried out using the Gaussian 09 quantum mechanics package and semi empirical calculations with Mopac (versions 2009) [22, 23]. The starting structures of β -CD and neurotransmitters were constructed with the help of the Cambridge ChemBio 3D Ultra (version 11.0, Cambridge software).

The method used by Liu and Guo was employed to find the minimum energy of the complex [24]. It also explores the conformational space along an axis passing through the center of the cyclodextrin cavity in which the neurotransmitter molecule is moved in respect of 1A in each displacement. Also, it is rotated by an angle equal to 20° [25]. The most stable structure was obtained at the optimum position and angle. This displacement of the guest molecule generates a number of conformations optimized by PM6 method (Parametric Method 6) [26]. Once the minimum energy structure is obtained, its geometry is re-optimized with ONIOM2 method [14].

In order to investigate the driving forces leading to the actual complex between the guest and the β -CD, we have to calculate the complexation energies, defined as the following:

$$E_{\text{complexation}} = E_{\text{complex}} - (E_{\beta-\text{CD}} + E_{\text{guest}})$$

The ONIOM energy is described as follows:

$$E_{ONIOM} = E_{complex, low} - (E_{CD, low} + E_{guest, high})$$

Chemometrics analysis, including MLR and PLS models were performed using the software MINITAB 16. The optimum number of PLS factors was determined by cross validation.

We subsequently applied the backward multiple linear regression (MLR) procedure in order to quantitatively relate the energy of complexation with the different properties by a mathematical expression.

We tested the electronic and steric properties of the neurotransmitters, which are classified as independent variables: With these independent variables, we attempted to explain the dependent variable, i.e. the energy of the complex. The values of these properties for the guest molecules and their inclusion complexes (DA: β CD, EP: β CD. S: β -CD, NA: β -CD, and AA: β -CD) are listed in Table 1.



Figure 1. General structure of catecholamines



Figure 2: Structure of ascorbic acid



Scheme 1. Chemical structures of natural cyclodextrin.

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Table 1: Electronic and hydrophobic properties of catecholamines and indolamines calculated B3LYP/6-31G (d) and their complexes with cyclodextrin

		Guest						Complex							
Complex ON	E _{complexat} ONIOM	Hydrophobic S properties p		Steric properties	Electronic properties				Electronic properties			Steric properties			
		$ \begin{array}{c c} Log & P_{th\acute{o}o} & Log \\ Hyperchem & P_{th\acute{o}o} \\ \end{array} $	Log	Volume	E _{HOMO}	E _{LUMO} (eV)	Gap E _{HOMO} -E _{LUMO}	μ(D)	E _{HOMO} (eV)	E _{LUMO} (eV)	Gap E _{HOMO} -E _{LU} мо	H bond			VDW
			P _{théo}	(cm ³ /mol)	(eV)							intra	intra inter		
			Marvin										ОНО СНО		
DA: β-CD	-38.71	-1.40	-0.33	120.08	-5.527	0.228	5.755	3.48	-8.633	3.722	12.355	1	2	1	3
p 02	-29.68								-8.528	3.356	11.884	1	1	2	1
EP:	-35.79	-1.61	0.85	128.34	-5.640	0.088	5.728	2.25	-8.356	3.493	11.849	5	4	4	3
β- CD	-14.80								-7.826	4.4635	12.290	2	0	2	0
NA: β- CD	-32.87	-2.02	-0.08	115.74	-5.598	0.084	5.682	2.14	-8.196	3.958	12.154	3	2	0	0
S: β-CD	-31.52	-2.21	1.23	134.66	-5.155	-0.084	5.071	3.16	-7.705	3.439	11.144	2	2	3	3
	-21.51								-7.350	3.833	11.183	0	1	1	1
AA:β-C D	-44.87	-2.44	-2.15	123.07	-6.508	-0.964	5.544	4.53	-9.739	2.829	12.568	2	3	2	0
	-40.18								-9.630	3.091	12.721	1	3	3	1

It is started by using a full model including all explanatory variables. Then, the statistical test H_0 is applied to eliminate variables with neither significant weight nor rich information in the model.

The quality of the generated models is determined by statistical measures: the square of the correlation coefficient (R^2) represents the part of variation in the observed data that is explained by the regression. F-test (Fisher's value) for statistical significance reflects the ratio of the variance explained by the model and the variance due to the error in regression [27]. The t-value is computed as the ratio between deviation from the mean accounted by a studied effect, and standard error of the mean. By comparing the t-value to its theoretical distribution (Student t-distribution), we obtain the significant level of the studied effect.

The p-value is also called the significance level. It is used to assess the significance of an observed effect or variation: a small p-value means that there is little risk of crediting artefactual effects. The usual limit used in the interpretation of a p-value is 0.05 (or 5%). If the p-value <0.05, there is no reason to believe that the effect is due to random variations. The effect must be significant [28].

Results and discussion

The inclusion complex has two orientations which will be denoted head and tail orientations. When the aromatic ring of guest molecule is inserted first into β -CD, we call this 'head orientation' and when the functional group is introducing first this orientation is known as 'tail orientation'.

The stabler structure can be obtained by comparing complex energies of these orientations. The values show that the inclusion complex of the head orientation is stabler than the tail orientation.

In all complexes, the geometry analysis of the most favorable orientation shows that the hydrophobic portion of the guest molecule is inside. In contrast to the hydrophobic cavity of the cyclodextrin, the hydrophilic parts are in the peripheral regions of the hydrophilic cyclodextrin.

In order to understand the stability of the complexes studied and to fix the main factors involving in the quantification of the complex energy, we tested the electronic and steric properties of the neurotransmitters. The following properties : the volume of the complex, hydrophobicity (log P), the E_{HOMO} , the E_{LUMO} , the gap E_{HOMO} - E_{LUMO} , dipole moment, number of inter-molecular hydrogen bonding, and the number of binding Van Der Waals, are classified as independent variables.

These independent variables are used to explain the dependent variable, i.e complex energy of the guest molecules and their inclusion complex (Table1)

The data listed in Table 1 is subject to several simple and multiple regressions.

The best MLR model is obtained by two variables: energy of both HOMO and LUMO of the studied complex.

The formula below explains the energy of the complex

 $E_{complexation} = 6.734 E_{HOMO} + 6.894 E_{LUMO} \dots (1)$

In which: E_{HOMO} and E_{LUMO} respectively are the HOMO and LUMO energies. The R² is the coefficient of determination in which R² =0.991, the Fisher's value (F) is equal to 197.39 and P-value is equal to 0.000.

The high correlation coefficient value obtained represents the best fit of the proposed regression. Since the F-value is high compared to tabulated values (5.41), the model is statistically significant.

For clear visualizing of the model's quality, we plotted the energy

of complex calculated by the ONIOM method and the energy that is calculated by the model (1).



Figure 3. Complexation energy calculated by ONIOM and the variation in the model

Figure 3 shows correlation between the complex energy calculated by ONIOM model energies and both E_{HOMO} and E_{LUMO} energies calculated by B3LYP/6-31G (d) method.

In this research work, PLS, a complementary method was used to predict ONIOM energy.

In PLS calibration models, the evaluation of the method linearity was carried out in order to show a proportional relationship between the complex energy calculated by the ONIOM method versus the energy of the PLS model.

The performance of the model was evaluated by the coefficient of determination R^2 and the root mean square error of cross validation RMSECV. In order to validate the model developed, cross validation using a 'leave one out' technique was used [29].

The PLS model offers a good correlation with R^2 of 0.987 in calibration and R^2 of 0.818 in prediction and a low RMSECV (RMSECV=3.767).

The Chemometric analysis demonstrates that the main variables selected to construct the PLS model corresponded to E_{HOMO} , E_{LUMO} (eV), Log P_{Marvin} , $\mu(D)$, The E_{HOMO} - E_{LUMO} gap of guest and VDW, and E_{HOMO} - E_{LUMO} gap of the complex.

Fig. 4 exhibits the scatter plot for the relationship between the energy of the complex calculated by the ONIOM method versus the energy calculated by PLS model.



Figure 4. Correlation plot of the predicted PLS energy versus energy ONIOM

As indicated in Fig.4, PLS was able to find a very good correlation with R^2 (0.988). The intercept and the slope of the predicted PLS energy vs. the ONIOM energy resulting in the following calibration data are 0.0000 and 1.0000 respectively. These results confirm the fitting quality of the model.

The model has an improvement equal to 3.20%, when it was applied to the validation set. Since the average cross validation error is below 11.57 %, an excellent prediction capability was observed.

The comparison between MLR and PLS models is illustrated by Fig.5.





Figure 5. Comparison of the energy ONIOM versus predicted PLS and MLR models.

As indicated in Fig.5, PLS and MLR models are powerful tools used to predict the ONIOM energy. The main factors that govern the stability of the studied complexes are E_{HOMO} , E_{LUMO} (eV), Log P_{Marvin}, μ (D), E_{HOMO} - E_{LUMO} gap of guest and VDW energy and E_{HOMO} - E_{LUMO} gap of the complex

Conclusion

We had studied the complexation of the each neurotransmitter molecule (catecholamines DA, NA and A, serotonin (S), and ascorbic acid AA) with β -cyclodextrin via the ONIOM method. From complexation energy, ONIOM results show that the head orientation is preferred. In this configuration, the catechol ring is deeply included into the hydrophobic cavity of β CD.

QSPR is used to find a quantitative relationship between the structure and the different properties to determine the factors affecting the complexation energy. The correlation studies of the complexation energies of different inclusion complexes helped to establish a relationship based on electronic and structural properties of guest molecules via linear regression. The proposed model, in which an excellent prediction capability was observed. is the one that is correlated to the frontier orbital energy of the complex.

The main factors that govern the stability of the studied complexes are E_{HOMO} , E_{LUMO} (eV), Log P_{Marvin}, $\mu(D)$, E_{HOMO} - E_{LUMO} gap of guest and VDW energy and E_{HOMO} - E_{LUMO} gap of the complex.

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References

- [1] Maseras, F. in: Cundari T.R. (Ed.), Computational Organometallic Chemistry, Marcel Dekker, New York, 2001, 159.
- [2] Dapprich S., Kom_aromi, I. Byun, K.S. Morokuma, K. Frisch, M.J. J. Mol. Struct. (THEOCHEM) 1999, 1, 461.
- [3] Maseras, F. Morokuma, K. J. Comput. Chem. 1995, 16, 1170.
- [4] Matsubara, T. Sieber, S. Morokuma, K. Int. J. Quantum Chem. 1996, 60, 1101.
- [5] Humbel, S. Sieber, S. Morokuma, K. J. Chem. Phys. 1996, 105, 1959.
- [6] Svensson, M. Humbel, S. Morokuma, K. J. Chem. Phys. 1996, 105, 3654
- [7] Svensson, M. Humbel, S. Froese, R.D.J. Matsubara, T. Morokuma, K. J. Phys. Chem. 1996, 100, 19357.
- [8] Dapprich, S. Koma´romi, I. Byun, K.S. Morokuma, K. Frisch, M.J. J. Mol. Struct. Theochem 1999, 461, 1.
- [9] Vreven, T. Morokuma, K. J. Comput. Chem. 2000, 21, 1419
- [10] Holt, J. S. J. Mol. Struct. 2010, 965, 31.
- [11] Attoui Yahia, O., Khatmi .D.E. J. Mol. Struct: THEOCHEM 2009, 912, 38
- [12] Huang M.J., Quan Z. and Liu Y.M. Int. J. Quantum Chem, 2009; 109(1): 81.
- [13] Benghodbane, S. Khatmi, D.E. J Incl. Phenom. Macrocycl. Chem. 2012, 15 (5), | 371.
- [14] Djemil, R. and Khatmi, D.E. Can. J. Chem. 2011, 89: 1519.
- [15] Vitaly Zhelezny, Vitaliy Sechenyh, and Anastasia Nikulina. J. Chem. Eng. Data, 2014, 59 (2), 485.
- [16] Xu Hui-Ying, Zou Jian-Wei, Hu Gui-Xiang, Wang Wei Chemosphere, 80, Issue 6, July 2010, 665.
- [17] Karelson M. (Ed.), Molecular Descriptors in QSAR/QSPR, Wiley-Interscience, 2000.
- [18] Fernandez, M. Caballero, J. Helguera, A.M. Castroe, E.A. Gonzalez, M.P. Bioorg. Med.Chem. 2005, 13, 3269.
- [19] Liane, S. Gonzalez, M.P. Fall, Y. Gomez, G. Eur. J. Med. Chem. 2007, 42, 64.
- [20] Kraim, K. Khatmi, D.E. Saihi, Y. Ferkous, F. Brahim, M. Chemometrics and Intelligent Laboratory Systems 2009, 97, 118.
- [21] Tropsha, A. Zheng, W. Curr. Pharm. Des. 2001, 7, 125.
- [22] Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Scuseria, G.E.; Robb, M.A.;
 Cheeseman, J.R.; Montgomery, J.A.; Vreven, Jr., T.; Kudin, K.N.; Burant, J.C.;
 Millam, J.M.; Iyengar, S.S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.;

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[23] Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J.E.; Hratchian, H.P.; Cross,

- J.B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R.E.; Yazyev, O.;
 Austin, A.J.; Cammi, R.; Pomelli, C.; Ochterski, J.W.; Ayala, P.Y.; Morokuma, K.; Voth, G.A.; Salvador, P.; Dannenberg, J.J.; Zakrzewski, V.G.; Dapprich, S.; Daniels, A.D.; Strain, M.C.; Farkas, O.; Malick, D.K.; Rabuck, A.D.;
 Raghavachari, K.; Foresman, J.B.; Ortiz, J.V.; Cui, Q.; Baboul, A.G.; Clifford, S.; Cioslowski, J.; Stefanov, B.B.; Liu, G.; Liashenko, A.; Piskorz, P.;
 Komaromi, I.; Martin, D.J.; Fox, T.; Keith, M.A.; Al-Laham, C.Y.; Peng, A.;
 Nanayakkara, M.; Challacombe, R.L.; Gill, P.M.W.; Johnson, B.; Chen, W.;
 Wong, M.W.; Gonzalez, C. and Pople, J.A. Gaussian 03, Revariision E01, Gaussian, Inc., Pittsburgh, PA, 2003
- [24] Stewart, J. J. P. J. MOPAC 2007; Stewart Computational Chemistry, Colorado Springs, CO, USA, 2007
- [25] Liu, L.; Guo, Q.X. J. Incl. Phenom. Macro. 2004, 50, 95.
- [26] Yan, C. L.; Li, X. H.; Xiu, Z. L.; Hao, C. J. Mol. Struct. THEOCHEM, 2006, 764 (1-3), 95.
- [27] Stewart, J.J.P. J. Mol. Model. 2007, 13, 1173
- [28] Pinheiro, L.M.V., Ventura M.C.M.M., Moita M.L.C.J. J. Mol. Liq., 154, 2010, 102.
- [29] Jahanbakhsh, G., Saadi, S., Steven, D. B. J. Mol. Struct. THEOCHEM, 2007, 805, 27.
- [30] Haaland, D.M.; Thomas, E.V. Anal. Chem. 1988, 60, 1993.

Ab-initio study of the structural and electronic properties of cadmium telluride CdTe and its alloy cadmium zinc telluride $Cd_{1-x}Zn_xTe$

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Abstract: The scope of this investigation is to make a clear contrast between the structural and electronic properties of cadmium telluride CdTe and its alloy cadmium zinc telluride $Cd_{1-x}Zn_xTe$ using first principles calculations based on density functional theory within the local density approximation (LDA). A supercell with $2\times2\times2$ unit cells has been considered in the calculations. Structural parameters and electronic densities of states are shown to discuss the effects of local environment induced by a Zn impurity on the structure of zinc-blende CdTe. Our results are in good agreement with other theoretical studies.

Key words: ab initio, DFT, electronic band structure, supercell, Vegard's law.

Introduction

The II-VI compounds have experienced a rather rapid development in recent years. They are materials which exhibit many interesting solid state phenomena of considerable practical importance [1-4]. These semi-conductor materials can crystallize in either the cubic zinc-blende (beta) phase (Figure 1) or the hexagonal wurtzite (alpha) phase. The compound CdTe can be considered as quite representative of this group. Indeed, the recent growing scientific and technological interest on CdTe arises from its peculiar physical properties, i.e. its mechanical, chemical and thermal stability. Moreover, CdTe is a promising material for electronic and optical devices [5]. Cadmium telluride (CdTe) is an excellent choice for use as a semi-conductor in solar panels because it is perfectly matched to the solar spectrum. It has proven to provide good optical performance over a wide temperature range and has provided a suitable mechanical robustness to be used as a substrate material. CdTe has a high resistance to moisture sensitivity, is available at a reasonable price and can operate at high filter deposition temperatures without disassociating. It is, however, also the softest of the II-VI materials and is most easily scratched or prone to cleaving. These characteristics provide the potential for high-efficiency modules, with low cost manufacturing processes [6-9].



Figure 1

The unit cell of CdTe in cubic zinc blende phase

The mixed crystals of II-VI compounds have attracted much attention in last few years. They are now used in a large variety of fields, including nuclear physics, X-ray and gamma ray astronomy and nuclear medicine. Among them we classify the cadmium zinc telluride ($Cd_{1-x}Zn_xTe$). Their great interest is mainly motivated by a promising series of applications in radiation detectors, solar cells and many other technological applications of general usefulness.

Vegard's law is assumed to be valid experimentally for the Cd $_{1-x}Zn_xTe$ alloys and often used to derive the Zn concentration but it is unclear whether "Vegard's law" [30], which assumes linear interpolation of the structural parameters, such as lattice constant and bulk modulus is valid in practice.

The structure of this paper is as follows: In section 2, we describe the calculation procedure. In section 3 we discuss the results obtained. Finally, a conclusion is given in section 4.

Computational details

The present calculations was carried out using the relativistic full-potential augmented-plane-wave (FP-LAPW) method in the framework of the Density Functional Theory (DFT) [10,11] incorporated in the Wien2k code [12,13] within the local density approximation (LDA) [14,15].

In the calculations the Cd ($4d^{10} 5s^2$), Te ($4d^{10} 5s^25p^4$) and Zn ($3d^{10}4s^2$) states are treated as valence electrons and the muffin tin radii values were fixed at 2.5 Bohr for all atoms. The *l*-expansion of the wave function were carried out up to $l_{max} = 10$ while the charge density was expanded up to $G_{max} = 12$ (Ryd)^{1/2} in a Fourier series.

The basis functions are expanded up to $R_{mt} \times K_{max}=9$ for both binary compound CdTe and its ternary alloy CZT (Were Kmax is the plane wave cut-off and R_{mt} is the

smallest Muffin Tin sphere radius). We then constructed $2 \times 2 \times 2$ supercells in the three directions (x, y, z) and we incorporate Zn atoms with different concentrations

and in different positions. We used a 10 10 10 Monkhorst-Pack mesh. The above parameters ensured an accuracy of 0.01 mRy in the total energy of the system.



Figure 2. Total energy versus volume for binary parent CdTe and its alloy Cd_{1-x}Zn_xTe

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Results and discussions

Structural properties

The structural properties are presented for the parent compound (CdTe) in the zinc blend structure and its ternary alloy $Cd_{1-x}Zn_xTe$ of composition x= 0.125, 0.25, 0.375, and 0.5. For each composition, we carried out a structural optimization by minimizing the total energy with respect to the cell volume and also the atomic positions.

To calculate the total energy as a function of volume followed by fitting the results with Murnaghan's equation of state [16], optimization of our compounds structures are done.

Were E_0 , B_0 and V_0 are respectively the total energy at equilibrium, the bulk modulus and the volume at equilibrium. From this fitting, the optimum lattice constant and bulk modulus are obtained. The variations of the total energy versus volume have been calculated for these compounds, the results are plotted in Figure 2. In Table 1 we show the LDA results regarding the equilibrium lattice constant a_0 , the bulk modulus B_0 and pressure derivative of the bulk modulus B'_0 in addition to the bandgap energy.

The present calculations within the LDA approximation, yield a slight underestimation of the lattice constant within 1.11 % and an overestimation of the bulk modulus around 2.31 % for binary compound in comparison with the experimental values. One can see from Figure 3a that the introduction of zinc in CdTe leads the lattice constant to decrease monotonically with composition following a decreasing linear function of composition x as expected by the Vegard's law, This agrees well with the results reported in Refs [17-20].

At low zinc concentration the calculated lattice constants are smaller than that predicted by the Vegard's law, while in the high-zinc-concentration region a positive deviation from Vegard's law is clearly visible [26].

One can see from Figure 3b a strong increase on the bulk modulus occurs in the low-zinc- concentration region, indicating that the Zn-Te bond embedded in the CdTe network is still stronger than the Cd-Te bond.

So a small addition of Zn to CdTe leads to a significant lattice contraction and produces dramatic bond relaxation to accommodate the radius difference between Cd^{+2} and Zn^{+2} , which is expected to create strain forces, thus inhibiting the dislocation motion and strengthening the Cd-Te bond in this materials [27], Moreover, the strongest bulk modulus from our results is around x= 0.35, supporting the speculation that the alloys with low Zn content have the significant stiffening as deduced from ion channeling measurements [28]. For higher Zn contents (x > 0.35) the bulk modulus decreases from x = 0.35 to x = 0.5. This trend holds in the high zinc-concentration region, where the stiff Zn-Te bond plays a dominant role in the

chemical bonding characteristics and leads to a reduction in the compressibility of the alloy lattice.



Figure 3. Calculated lattice constants (a) and bulk modulus (b) as a function of composition x for $Cd_{1-x}Zn_xTe$

Table 1. calculated structural an	d electronic pa	rameters for	CdTe binary	compound
and its alloy $Cd_{1-x}Zn_xTe$.				

	Cd	Ге	Cd _{1-x} Zn _x Te				
this	r work Ex	Other cal	x	Eg(eV)		$a_0(A^{\bullet})$	
structur	ral and elect	tronic parameters	this work	Other cal Other cal	Exp Exp	this work	
$a_0(A^\circ)$	6.41 ,6.42 ^b	6.43 ^a	0.125 0.466	12.819	-	-	
$B_{0(GPa)}$	45.53	46.0 ^a 44.5 ^a	0.25 12.748	$5.98^{ m f}$ 0. 265	-	0.48 ^f	
<i>B'</i> 4.8	0 38	4.60^{e} 6.40^{a}	0.375 12.654	- 0.319	-	-	
Eg(eV)	0.601	0.64^{b} 1.56^{d} 0.60^{c}	0.5 12.596	5.876 ^f 0.025	-	$1.01^{\rm h}$ $1.92^{ m g,h}$ $0.62^{ m f}$	

a [Ref 21], b[ref22], c[ref23], d[ref24], e[ref25], f[ref31], g[ref32], h[ref33]

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Electronic properties

To investigate the electronic properties of CdTe as well as its alloy, we have calculated the band structure within the LDA method using equilibrium lattice constants as obtained previously. For the binary compound the valence band maximum (VBM) and the conduction band minimum (CBM) occur at the Γ point; hence this compound is a semi-conductor with a direct band gap Γ - Γ . Our results are compared with experimental values and other theoretical results in Table 1. It is well known that calculation using LDA underestimates the band-gap values of III-V and II-VI semiconductors. The band gap value obtained for CdTe compound is smaller than the experimental one, but it agrees well with other theoretical results.

For the first concentration (x=0.125) we noticed from the band gap structure that our alloy is a semi-conductor with an indirect Γ - Δ band gap (0.466 eV) followed by Γ - Λ (0.472 eV). The other values for different concentrations x are showed in the table 1. To the best of our knowledge there are no theoretical or experimental data for many concentrations to check our predicted results. In previous calculations [31] the gap energy value decreased slightly for low Zn concentration (x< 0.5) and beyond 0.5, it increases rapidly.

It is now admitted that the ternary alloys have a parabolic compositional dependence for their gaps. The magnitude of the parabolic factor is known as the bowing. Experiments are carried out at different temperatures. They show significant variation of this bowing factor with temperature. No temperature effect has been included in the above calculations. They should be compared with data taken at low temperature whenever possible. We note a contradiction especially in the energy gap value of x=0.5 in concentration. This is very small in comparison with the other gap values. There is a slight difference between many calculated results in the literature because of the method used and the size of the supercell constructed. However, note that several important features in the experimental data are reproduced by the calculation.

The band structure and the total DOS of CdTe are represented in Figure 4. The band structures of CZT alloys are represented in Figure 5.



Figure 4. Electronic band structure and total DOS of CdTe .

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Figure 5. Electronic band structures of $Cd_{1-x}Zn_xTe$ for different *x* concentrations.

Conclusion

In summary, using the FP-LAPW method we have studied the structural and electronic properties of the binary parent semiconductor CdTe and its alloy CZT. We show the lattice constants of CdZnTe closely follow Vegard's law. The variation in the bond lengths causes a slight deviation in the lattice constant. The ordering at low concentration of Zn needs the intermixing of Cd and Zn elements and rearrangement of atoms. This is induced by the long time and the high temperature of the annealing of the samples [17]. Charge exchange between Cd, Zn and Te atoms acts as a driving force that tends to stabilize these alloys. From the electronic parameters we can conclude that the alloy CdZnTe is a semiconductor compound, where the low x concentration is not very influential on the band gap energy value. We also must take into account the role of the calculation method used. It is well known that calculation using LDA underestimates the band-gap values of III-V and II-VI semiconductors

References

- [1] M. Aven, J.S. Prener, Physics and Chemistry of II-VIcompounds, North-Holland, Amsterdam, 1976.
- [2] L. Ley, R.A. Pollak, F.R. McFeely, S.P. Kowalczyk, D.A. Shirley, Phys. Rev. B 9 _1974. 600.
- [3] M.A. Hasse, J. Qui, J.M. Deluydt, H. Cheng, Appl. Phys. Lett. 59 _1991. 1272.
- [4] H. Kinto, M. Tanigashira, T. Yamada, H. Uchiki, S. Lida, J.Cryst. Growth 117 _1992.
 348.
- [5] M.H. Kruse, in: R.K. Willardson, A.C. Beer _Eds.., semiconductors and semimetals, Academic, New York, 1981, vol. 16, p. 119 and vol. 18, p. 1.
- [6] P. Capper (Ed.), Properties of Narrow Gap Cadmium-Based Compound, GEC Marconi Infra-Red Ltd., Southampton, UK, ISBN 0-85296-880-9, 1994.
- [7] D.W. Palmer, Properties of the II-VI Compound Semiconductors, /www.semiconductors.co.ukS, June 2002.
- [8] National Renewable Energy Laboratory (NREL). Cadmium Use in Photovoltaic, /www.nrel.govS.
- [9] Environment CdTe Technology, /www.firstsolar.com/environment_cdte.phpS.
- [10] Hohenberg P., Kohn W. Inhomogeneous electron gas // Phys. Rev. 1964. 136. P. B864.
- [11] Kohn W. Sham L.S. One-particle properties of an inhomogeneous interacting electron gas // Phys. Rev., 1965. 140. P. A1133.
- [12] P. Blaha, K. Schwarz, G.K.H. Madsen, D. Kvasnicka, J. Luitz, WIEN2k, An Augmented Plane Wave + Local Orbitals Program for Calculating Crystal Properties, Karlheinz Schwarz, Techn. University at, Wien, Austria, 2001, ISBN 3-9501031-1-2.
 [13] M. Peterson, F. Wagner, L. Hufnagel, M. Scheffler, P. Blaha, K. Schwarz, Comput. Phys. Commun. 126 (2000) 294.
- [14] P. Hohenberg, W. Kohn, Phys. Rev. 136 (1964) 864.
- [15] W. Kohn, L.J. Sham, Phys. Rev. A 140 (1965) 1113
- [16] Murnaghan, F.D., 1944. Proc. Natl Acad. Sci. USA 30, 244

- [17] Arbaoui A., Outzourhit A., Achargui N. et al. Effect of the zinc composition on the formation of ternary alloy Cd1-*x*Zn*x*Te thin films // Sol. Ene. Mater. Sol.-Cells. 2006. 90. P. 1364.
- [18] Ammar A.H. Studies on some structural and optical properties of Zn*x*Cd1-*x*Te thin films // App. Surf. Sci. 2002, 201. P. 9.
- [19] Soliman H.S., Allam F.M., El-Shazily A.A. Structural and optical properties of Cd1-*x*Zn*x*Te thin films // J. Mater. Sci. Mater. Elect. 1996. 7. P. 233.
- [20] Schenk M., Hähnert I., Duong L.T.H. et al. Validity of the lattice-parameter Vegard-rule in Cd1-*x*Zn*x*Te solid solutions // Crys. Res. Tech. 1996. 31. P. 665.
- [21] Semiconductors, Physics of Group IV Elements and III-V Compounds, edited by K. H. Hellwege and O. Madelung, Landolt-Börnstein, New Series, Group III, Vol. 17, Pt. a (Springer-Verlag, Berlin, 1982); Semiconductors, Instrinsic Properties of Group IV Elements and III-V, II-VI, and I-VII Compounds, edited by K. H. Hellwege and O. Madelung, Landolt-Börnstein, New Series, Group III, Vol. 22, Pt. a (Springer-Verlag, Berlin, 1982).
- [22] A Shepidchenko, S Mirbt, B Sanyal, A H°akansson and M Klintenberg. J. Phys.: Condens. Matter 25 (2013) 415801.
- [23] Carvalho A, Tagantsev A K, O" berg S, Briddon P R and Setter N 2010 Cation-site intrinsic defects in Zn-doped CdTe Phys. Rev. B 81 075215.
- [24] Lutz G 1999 Semiconductor Radiation Detectors. Device Physics (Berlin: Springer)
- [25] A.E. Merad, M.B. Kanoun, G. Merad, J. Cibert, H. Aourag, Mater. Chem. Phys. 92 (2005) 333.
- [26] R. Miloua, F. Miloua, A. Arbaoui, Z. Kebbab, N. Achargui, N. Benramdane. International Scientific Journal for Alternative Energy and Ecology № 6 (62) 2008.
- [27] K. Guergur, R. Triboulet, A. Tromson-Carli, Y. Marfaing, J. Cryst. Growth 86 (1998).
- [28] D. Comedi, R. Kalish, Phys. Rev. B 46 (1992) 1584461.
- [29] He Duan, Xiaoshuang S. Chen *, Yan Huang, Liang Wang, Wei Lu. Physics Letters A 370 (2007) 517-521.
- [30] Vegard, "Formation of Mixed Crystals by Solid-Phase Contact," *Journal of Physics*, Vol. 5, 1921, pp. 393-395.
- [31] Mohammed Ameri, Meriem Fodil, Fatma Zahra Aoumeur-Benkabou, Zoubir Mahdjoub, Fatima Boufadi1, Ali Bentouaf. *Materials Sciences and Applications*, 2012, 3, 768-778.
- [32] Brasil M J S P, Tamargo M C, Nahory R E, Gilchrist H L and Martin R J 1991 Appl. Phys. Letr. 59 1206
- [33] H C Poont, Z C Fengt, Y P Fengt and M F Li. I. Phys.: Condens. Matter 7 (1995) 2783-2799. Printed in the UK

Conformational Analysis and Rationalization of the Observed Enantioselecvtivity in the Corey-Bakshi-Shibata Reduction: A DFT/B3LYP Study

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Abstract: Theoretical studies on the conformation of the most favorable transition states of *Re*- and *Si*- type of the parent oxazaborolidine have been performed by means of the Density Functional Theory (DFT) method. The *syn/anti* term refers to the value of the dihedral angle H-B-O=C (nearly 0° in *syn* complexes and nearly 180° in *anti* ones). The results suggested low energy conformations for those complexes that could be useful in further parameterizations for structural modeling studies. A set of conformations for the acetophenone–CBS–BH₃ complexes were characterized at the B3LYP/6-31G (d,p) level and it was found that the picture obtained depends heavily on whether the *syn* or *anti* conformations prevail. A computational strategy for identifying the hydride transfer from the BH₃ moiety on the *Re* and *Si* face of the carbonyl substrate, which takes place via a six-membered transition state, was developed and tested, using a model system for which the transition state geometry was already known. The DFT method predicts that the planar and non planar *syn/Re* forms are slightly more stable than *anti/Re*.

Keywords: Internal rotation, Dihedral angle, Acetophenone, Oxazaborolidine, syn, anti, B3LYP.

Introduction

In 1987-88, Corey, Bakshi, and Shibata (CBS) constructed a new class of structurally rigid oxazaborolidines, which they used in catalytic quantity for the reduction of pro-chiral ketones, and defined the reducing species. They proposed for the first time that the reducing agent is an oxazaborolidine, as well as giving its mechanism of action.[1-3] The second generation oxazaborolidine by Corey, Bakshi, and Shibata is capable of reducing a great variety of ketones under mild reaction conditions, with quantitative yields and excellent enantiomeric excesses. Moreover, the CBS catalyst (so-called after the names of its inventors) bearing a methyl substituent at the endocyclic boron shows more stability, allowing it to be weighed in the open air. The reduction products, optically pure alcohols and their derivatives have various applications, especially in medicinal chemistry and organic synthesis [4-7].

While excellent mechanistic work by Corey's group [1-3, 8] and others [9-12] has yielded a satisfying picture of the catalytic cycle for CBS reductions (Scheme1), an experimentally-validated picture of the transition structure corresponding to the rate-determining step is lacking. From а mechanistic point of view. the oxazaborolidine-mediated reduction of ketones bears some characteristics: in the reaction, a heterocyclic five membered ring formed from an amino alcohol and the corresponding reagent act as a dissymmetric template onto which the reacting molecules coordinate. These templates present a central heteroatom with Lewis acid character (boron) flanked by two atoms with Lewis base character. During the reaction, it is assumed that coordination of the carbonyl compound takes place at the Lewis acidic site, and the main difference between the reacting complexes lies in the Lewis base atom type, involved the reagent coordinates: borane and nitrogen.



Scheme 1. Catalytic Cycle of the CBS Reduction

It is widely accepted that oxazaborolidines, through their adjacent boron and nitrogen atoms with complementary Lewis acid and Lewis base character, can give rise to complexes incorporating one borane and one ketone molecule in a very favorable arrangement for this arrangement reaction. In this process, the role of the substituents at the carbon atoms of the oxazaborolidine ring (those of the starting amino alcohol) is that of directing the complexation of the reactants toward the less hindered diastereotopic face of the oxazaborolidine ring. When a pro-chiral ketone (R_LCOR_S) is involved in the process, four possible geometries (syn/Re, syn/Si, anti/Re, and anti/Si) can exist for these complexes (Fig.1 and 2) depending on the oxygen lone pair involved in the complexation and the enantiotopic face of the carbonyl compound offered to the BH3 moiety. In their names, the syn/anti term refers to the value of the dihedral angle CH₃-B-O=C (nearly 0° in syn complexes and nearly 180° in anti ones), whereas Re/Si refers to the face topicity of the carbonyl group opposite to the BH₃ moiety. The anti/Re and syn/Si complexes offer the Si face for hydride attack. In the anti/Si and syn/Re complexes of acetophenone, the exposed face is the Re face (Fig.1), which leads to the product that is preferentially formed in the experiment. At least one transition state stemming from these two complexes must be thus determine the outcome of the reaction.

In the present instance, we studied at the DFT level of theory the possible modes of complexation of 1-phenylethan-1-one with the borane adduct of $CBS-CH_3$, as well as the derived transition states, in agreement with the commonly accepted reaction mechanism.

Stability differences between the *syn* and *anti* conformers are very subtle. This work reinvestigates the whole problem in a more systematic manner than has been done before.



Figure 1. Schematic representation of the two possible reactive complexes in the oxazaborolidine-mediated reduction of acetophenone with borane selected as the model reaction,



Figure 2. Computed transition structures [B3LYP/6-31G(d,p)] of the *Re*- and *Si*-type conformations. Phenyl groups on the (*S*)-CH₃-CBS catalyst are indicated by gold spheres.

Computational methodology

All calculations of the key steps in the CBS-catalyzed reduction of acetophenone were carried out in vacuo with the Gaussian 03 (G03) package¹³ using density functional theory with the hybrid B3LYP^{14,15} functional and 6-31G(d,p) basis set. The internal rotational angle (θ) is defined as the C-B-O=C dihedral angle. The conformational relative energies were obtained by performing geometry optimization calculations at a set of selected θ values scanning from 0 to 360 degrees in 20-degree steps. The gas-phase standard enthalpy of formation of molecule *j* at 298.15 K and can be determined from the equation:

$$\Delta_{f}H^{o}(\mathbf{M}, 298\mathbf{K}) = \sum_{atoms} x \Delta_{f}H^{o}(\mathbf{X}, 0\mathbf{K}) - 627, 5095 \left[\left(\sum_{atoms} x \mathcal{E}_{0}(\mathbf{X}) - \mathcal{E}_{0}(\mathbf{M}) \right) - \left(H_{corr} - \mathcal{E}_{ZPE}(\mathbf{M}) \right) \right] - \sum_{atoms} x \left(H_{X}^{o}(298\mathbf{K}) - H_{X}^{o}(0\mathbf{K}) \right)$$

Where *x* is the number of atoms *X* in molecule *M* and H_{corr} is the thermal correction to Enthalpy. $\mathcal{E}_{O}(M)$ and $\mathcal{E}_{ZPE}(M)$ denote, respectively, the total energies of the molecule and zero-point energy of the molecule, calculated using the Gaussian 03 software package. The units are Hartree molecule⁻¹ for $\mathcal{E}_{O}(M)$, $\mathcal{E}_{ZPE}(M)$, and thermal corrections, whereas $\Delta_{f}H_{298.15K(g)}^{o}$ is in kcal mol⁻¹ (1 Hartree = 627.5095 kcal/mol).

	Atom		$\Delta_f H^o(M, 0K)$
$H_X^o(298 \text{K}) - H_X^o(0 \text{K})$			
Н		51.63 ± 0.001	
1.01			
	В		136.2 ± 0.2
0.29			
	С		169.98 ± 0.1
0.25			
	Ν		112.53 ± 0.02
1.04			
	0		58.99 ± 0.02
1.04			

Table 1. Experimental enthalpies of formation of elements (kcal mol⁻¹) [16].

Results and Discussion

The computational study of the key steps in the CBS-catalyzed reduction of acetophenone were carried out in vacuo by means of DFT calculations.

It is important to mention here that the decision to only perform the conformational analysis on the dihedral θ described in this work was supported by the following reasons: Energetically, θ is the dihedral angle related to the highest energy points in the acetophenone (PhMK) and CBS–BH₃ complex, consequently, to the highest barriers of energy, Variations of these dihedral angles intensify repulsions between two or more groups. like aromatic rings and methyl, BH₃ groups. In order to avoid poor parameterizations and, consequently, trapping the molecule in local minima, it is of fundamental importance to obtain information about putative minima obtained by the conformational analysis of these angles. Variations in the other dihedral angles in (*S*)-H-CBS catalyst do not cause strong enough steric effects to cause problems in further parameterizations.

The B3LYP/6-31G (d,p) conformational analysis for *Re*-and *Si*-type transition states are shown in Fig. 3. The conformational analysis for the two complexes is described as follows. Along the θ dihedral variation from 0 to 360 degrees there exist the planar and non planar *syn* minima (at θ =300 - 40) and the *anti* minima (emerges with a possible deviation from planarity by no more than -10° with *Re*-type and no more than +30° with *Si*-type) (stable conformers) and two transition states. One transition state denoted as *TS1* appears between the *syn* and *anti* minima and another denoted *TS2* appears between the *anti* and *syn* minima. The *syn* minimum is lower than the *anti* minimum, and *TS1* is higher in energy than *TS2*. The *anti* conformers of the *Re*- and *Si*-type transition states are located at the θ values of 170°, 210°,

respectively, the *TS1* conformers of the *Re*- and *Si*-type transition states are located at the θ values of 120°, 140°, respectively, and the *TS2* transition states of the two complex type are located at the θ values of 200°, 240°, respectively.

The energetic barrier to θ variation around the B-O bond that has its maximum at 200° for the *Re* conformer and at 240° for the *Si* conformer were predicted to be of moderate height, -610.0 and -732.0 kcal mol⁻¹, respectively, whereas the barrier that has its top at 120° for *Re* conformer and 140° for *Si* conformer should, according to the calculations, be considerably higher, 220.0 and -213.0 kcal mol⁻¹, respectively. Despite this, the energy conformation increases faster when the system changes from the minimum-energy conformation for *Re*-type transition states (compare, for example, the energies corresponding to the C-B-O=C values at 160 and 180°, Fig. 3), and the energy conformation increases faster when the minimum-energy conformation 210° toward the 240° conformation for *Si*-type transition states (compare, for example, the energies at 200 and 220°, whereas the energy conformation increases faster with *Re* conformer (than with *Si*) when the system changes from the minimum-energy conformation 0° towards the maximum (Fig. 3).

For each of the two types transition states (*Re* and *Si*) the relative energies of the *syn*, *anti*, *TS1*, and *TS2* conformers of *Re*-type are predicted to be -863.0, -783.0, 220.0 and -610.0 kcal mol⁻¹, respectively, and of *Si*-type the relative energies are predicted to be -862.0, -796.0, -213.0 and -732.0 kcal mol⁻¹, respectively. For the analysis of the variation of the θ dihedral angle (Figure 4), the barrier heights for the *syn* \rightarrow *TS1* processes are evaluated to be 1083.0 and 649.0 kcal mol⁻¹ for Re- and *Si*-type transition states, respectively, and the barrier heights for the *TS1* \rightarrow *anti* processes are evaluated to be 1003.0 and 583.0 kcal mol⁻¹ for Re- and Si-type transition states, respectively, and the *syn* (at θ =300-40°) conformers are more stable than *anti*.

The barrier with maximum at the TS1 conformation of Re- and Si-transition states are as high as 220.0 and -213.0 kcal mol⁻¹, respectively, whereas that corresponding to the TS2conformation are only -610.0 and -213.0 kcal mol⁻¹, respectively. This large difference in the energy barriers could be expected because for the 120° with Re-type and for the 140° with Si-type transition states conformations the repulsions between the CH₃ group of the acetophenone and BH₃ moiety and between the phenyl group of the acetophenone and BH₃ moiety, respectively, on side of the molecule, should be significantly stronger in comparison

to the repulsions between the CH₃ group of the acetophenone and oxygen lone electron pair in the 200° conformation for *Re*-type transition state, and between the phenyl group of the acetophenone and oxygen lone electron pair in the 240° conformation for *Si*-type.

As a consequence of this finding, the syn/Re conformation is slightly more stable (the low-energy conformers) than the syn/Si conformers and the anti/Si is much more stable than the anti/Re. Therefore the theoretical calculation reported here predict that the reduction with borane of acetophenone as a model substrate of prochiral ketones mediated by oxazaborolidine will preferentially lead to phenylehan-1-ol of R configuration, as is experimentally observed [8, 17].



Dihedral angle/degrees



Figure 3. DFT(B3LYP)/6-31G(d,p)-calculated conformational relative energies of acetophenone (PhMK) and CBS-BH₃ complex with θ dihedral variation from 0 to 360 degrees.

Conclusions

In this investigation we have presented DFT calculations on geometries and energies for the θ dihedral variation of acetophenone (PhMK) and CBS–BH₃ complex from 0 to 360 degrees. Along the θ dihedral variation there exist the planar and non-planar *syn*, *TS1*, *anti*, and *TS2* transition states. Our interest concentrated on the question whether the *syn* or the *anti*, the *syn*/*Re* or the *syn*/*Si*, and the *anti*/*Re* or the *anti*/*Si* conformer is the more stable one. In our calculations the planar and non-planar *syn* (at θ =300-40°) arrangement of *Re*-type transition states is slightly more stable than the *syn* arrangement of *Si*-type and the *anti*/*Si* conformer (with a tolerance of +30° in the deviation from planarity) is much more stable than *anti*/*Re* conformer (with a tolerance of -10° in the deviation from planarity).

References and Notes

- [1] E.J. Corey, R.K. Bakshi, S. Shibata, J. Am. Chem. Soc. 1987,109, 5551
- [2] Corey, E. J.; Bakshi, R. K.; Shibata, S.; Chen, C.-P.; Singh, V. K. J. Am. Chem. Soc. 1987, 109, 7925-7926.
- [3] Corey, E. J.; Bakshi, R. K.; Shibata, S. J. Org. Chem. 1988, 53, 2861-2863.
- [4] S. Miyano, L.D. Lu, S.M. Viti, K.B. Sharpless, J. Org. Chem. 1985, 504350.
- [5] P.A. Chaloner, E. Langadianou, *Tetrahedron Lett.* **1990**, 31, 5185.
- [6] K. Soai, S. Yokoyama, T. Hayasaka, J. Org. Chem. 1991, 56, 4264.

- [7] E.J. Corey, C.J. Helal, *Tetrahedron Lett.* **1997**, 38, 7511.
- [8] Corey, E. J. Pure Appl. Chem. 1990, 62, 1209-1216.
- [9] Jones, D. K.; Liotta, D. C. J. Org. Chem. 1993, 58, 799-801.
- [10] Mathre, D. J.; Thompson, A. S.; Douglas, A. W.; Hoogsteen, K.; Carroll, J. D.; Corley, E. G.; Grabowski, E. J. J. J. Org. Chem. 1993, 58, 2880-2888.
- [11] Linney, L. P.; Self, C. R.; Williams, I. H. J. Chem. Soc., Chem. Commun. 1994, 1651-1652.
- [12] Jockel, H.; Schmidt, R.; Jope, H.; Schmalz, H.-G. J. Chem. Soc., Perkin Trans. 2. 2000, 69-76.
- Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; [13] Cheeseman, J. R.; Montgomery, J. A.; Vreven, T., Jr.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. GAUSSIAN 03, Revision C.02; Gaussian, Wallingford CT, 2004.
- [14] Becke, A. D. J. Chem. Phys. 1993, 98, 5648-5652.
- [15] Lee, C.; Yang, W.; Parr, R. G. Phys. Rev. B. 1988, 37, 785-789.
- [16] Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Pople, J. A. J. Chem. Phys. 1997, 106, 1063.
- [17] E. J. Corey, M. Azimora, S. Sarshar, Tetrahedron Lett. 1992, 33, 3429-3430.

Theory and simulation of selective hydrocarbon oxidation at copper surfaces: Part I methane mild oxidation to methanol, formaldehyde and formic acid

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Abstract: This work follows a fundamental study, by density functional theory (DFT) coupled to Monte Carlo simulations of oxygen diffusion at nanostructured Cu(100) compared to electron microscopy images. It was shown that partial oxydation of this copper surface occurs readily and is facilitated by defects.

Previous work by a number of authors, using DFT, highlights partial oxidation, especially of methanol on copper and also methane de-hydrogenation on a number of catalysts, mostly involving precious metals. Here we demonstrate the usefulness and selectivity of a cheap catalytic system. It comprises partially oxidised Cu(100), synthesized as described above.

The major reaction is methane to methanol, which occurs readily at 300K. We also show that methanol is re-adsorbed and oxidised to formaldehyde, as also observed by Stampfl. This reaction is somewhat hampered by the formation of surface methoxy species, that may poison the catalyst at low temperatures. Formaldehyde may be oxidised further to formic acid, under pressure.

The complete oxydation product, CO₂ was absent from these systems.

Introduction.

This work describes mild oxidation of methane to methanol, formaldehyde and formic acid.

These partial oxidation reactions (i.e. avoiding CO_2 as product) are selective on paladium (100) or rhuthenium-doped copper.

The expense of these efficient catalysts is the driving force for investigating cheap alternatives, based on copper. This work reports partial oxidation of Cu(100) and its subsequent selective use as a mild oxidation catalyst. It is the first part of DFT/Car-Parrinello woek on selective oxidation. The second part follows on in the present volume and reports on selective epoxidation of alkenes.

Use of plane-wave Density functional theory

The theory level chosen is Density Functional Theory (DFT) within the Generalised Gradient Approximation (GGA) [1]. First, we should point out that DFT is in principle exact. The ground-state energy of any system can be written as a unique functional of the total electron density. This is a powerful formalism, because the density includes the electronic interactions and electron correlation. Determination of ground-state energy must be carried out recursively since the total electron density is usually evaluated from one-electron wave-functions or spin-orbitals that are eigenfunctions of a one-electron Hamiltonian. This explains how the Kohn-Sham formalism is introduced and, with it, approximation. If the electron energy could be written down or determined first, then it could be improved recursively to give exact ground-state properties. This is not possible except for a few 'toy' systems, like the uniform electron gas, which although simple, has been used as a model for metallic systems and also a means to provide initial densities for the Kohn-Sham equations. In these single-particle equations, part of the electronic external potential is a (generally unknown) functional of the total electron density. This is the exchange-correlation potential. Note that the Kohn-Sham hamiltonian is truly a one-electron operator and its eigenfunctions are spinorbitals which involve one electron at a time and the matrix elements do not include exchange integrals. Some hybrid functionals take Hartree-Fock exchange into account (in the Hartree-Fock formalism, a double sum over electron indices allows exchange integrals to be evaluated exactly in an atomic orbital basis). The Kohn-Sham formalism collects the parts of the potential that each electron feels and which cannot be evaluated in a one-electron formalism to form the exchange-correlation potential. It is then expressed as a functional of the total electron density. Many possible choices of functional have been applied and we discuss our choice in the next section.

Since this application involves solids truncated by a surface, it is opportune to use a formalism appropriate to periodic systems [1]. This involves expanding the spinorbitals in a plane-wave basis evaluated numerically over a grid of points. The grid is generally not set up in real space since reciprocal space is convenient for defining the first Brillouin zone for solids. The definition is extended to surfaces, even with adsorbed molecules, by retaining true periodicity in the two dimensions parallel to the surface and imposing it artificially in the perpendicular direction by leaving sufficient vacuum spacing between the finite solid 'slabs' possibly complete with adsorbed molecular systems. This leads to larger unit cells and often longer calculations. The grid is defined by the number of sampled k-points i.e. numerical values that define the three k-vector components in reciprocal space (for the first Brillouin zone). It often needs to be quite a dense grid like 16 16 1. A single point in the perpendicular direction is enough. The vacuum spacing needs to be large enough to avoid artefactal interactions between slabs.

The kinetic energy cutoff must be high enough to include all k-vectors significantly contributing to the energy. This finite value determines the speed of calculations but must be chosen on a physical basis which relates to the speed electrons may have.

In practice, for systems of this size, all electron calculations would be prohibitive in computer time. The core-electrons are therefore just represented by a function known as a pseudo-potential that must be evaluated in advance for a given functional.

Choice of functional and use of pseudo-potentials.

Functionals describe the analytical dependence of exchange-correlation potentials on total electron density. The simplest category adopt the local density approximation (LDA) which provides functionals depending only on the density (a spin density form, Local Spin Density is mostly useful for magnetic properties).

In the Generalised Gradient Approximation, the functional depends on the density and its gradient (sometimes with respect to several parameters). Our choice is within this GGA approximation and called the PBE functional, originally introduced by Perdew, Burke and Enzerhof [2]. We have made this choice because the functional is free of parameters fitted to experiment and can therefore be considered to be *ab initio* which is quite unusual for DFT. The parameters are fundamental constants of physics and numerical values obtained by extrapolating to low-density limits giving the uniform electron gas. Nothing empirical is used.

The copper atoms would have Z=29 in an all-electron treatment which would already be prohibitive since we use at least 23 Cu atoms (5 layers, with 5, 4, 5, 4 and 5 atoms exposing the 100 face). An Ar-core pseudo-potential from the Fritz Haber institute is used. It is based on the Troullier-Martins soft potential scheme (that screens less than an 18-electron charge portion of Z) and formally leaves 11 electrons per neutral Cu-atom. The imperfect screening means that average electron kinetic energy can be quite high and the kinetic energy cutoff (ecut) required for accurate work is also high. We used ecut=80 Ha.

The corresponding pseudo-potential is used for the atoms H, C and O. In the case of H, it is not a physical necessity but facilitates energy calculations and in the case of the first-row elements it is a soft He-core. Nevertheless, Cu is the easiest of the atoms involved to ionise and thus determines the suitable value of ecut.

Geometry optimisation

To implement the Kohn-Sham formalism it is necessary to separate fast electron motion from slow nuclear motion. This separates the Hamiltonian within the Born Oppenheimer approximation that is implemented here as the 'clamped nucleus' approximation, where, not only is the nuclear kinetic energy much lower than its electronic counterpart but their positions are fixed, making it zero. For a fixed nuclear geometry, the electronic hamiltonian is solved in the Kohn-Sham one-electron formalism.

The geometry can be relaxed. This is done by calculating the first derivatives of ground-state energy and modifying them according to estimated force constants, based on approximate second derivatives until a minimum of energy is found. At this point, the first derivatives of energy may fall below a small threshold value. The procedure used tends to lead to the closest minimum to the input co-ordinates, simply because once the minimum

criterion has been reached, the process stops. This prevents users from finding lower minima that require more variation of geometry.

Car-Parrinello dynamics to follow a reaction path

The local minimum trap problem can be avoided by using molecular dynamics approaches that simulate annealing, i.e. a (random) kinetic energy is added to the system so that its nuclei move and its energy increases. It is quenched from this high-energy state, falling into a lower energy and modified geometry. This can be done progressively (by freezing some co-ordinates and varying others) to follow a reaction from reactants to products. Car-Parrinello dynamics were used [3].

The idea is to convert the time-dependent system into Lagrange dynamics by making suitable approximations, the key one being to ascribe a fictitious mass to the electronic wave-function in order to move from one geometry treated in the Kohn-Sham formalism to another in a semi-classical Euler-Lagrange dynamic approach. This considerably reduces the calculation time compared to solving the time-dependent problem fully and can be used to follow a reaction path, with electron transfer (that must be determined by fixed-geometry solution of the Kohn-Sham equations at regular intervals) nevertheless.

Software implementations used.

Plane-wave DFT is implemented in a number of software packages. This work uses the freeware ABINIT on a parallel PC cluster. It draws from PhD results by one of us [4].

Results

Methane is oxidised to methanol. Activity is optimal for a partially oxidised Cu(100) surface. This surface forms from clean Cu(100) in the presence of low pressure gaseous oxygen molecules. Oxidation is less than a monolayer coverage and defects or steps are involved [5].



Methane (physisorped)







HO bond (initial)



Finally, proton transfer occurs to the copper and methanol is desorbed. The partially oxidised Cu(111) surface is restored (as required for catalysts), in the presence of molecular oxygen.





During the proton transfer step, this surface may form methoxy radicals from methanol that are strongly adsorbed, taking no further part in the oxidation process. The surface methoxy groups tend to accumulate, poisoning the catalytic surface. They may be desorbed by heating.

Further oxidation occurs to formaldehyde and formic acid.



Formaldehyde (physisorped)



Formaldehyde O-O forms

Formaldehyde is formed by de-hydrogenation of methanol. The copper forms Cu-H linkages before desorbing hydrogen gas. This process was also extensively studied in [6] on supported copper. Formaldehyde re-adsorbs at an oxygen site which oxidises it before a final deprotonation.



Formate (CH₂O oxydation)



Formate CuO interaction (catalytic effect)



Free formate

Formaldehyde is readily oxidised by the Cu(100) after an oxygen atom is transferred from the partially oxidised copper. CuO linkages maintain low barriers. Final proton transfer gives HCOOH (formic acid) but no CO_2 is observed.

Discussion and conclusions.

Previous DFT studies have treated methanol partial oxidation on copper, with similar results [6] and similar work on precious metal-based catalysts also shows selective oxidation of methane, mostly giving formaldehyde [7, 8]. A recent comparative DFT study on methane catalysts [9] includes various copper systems with adsorbed methane dehydrogenation, but not Cu(100) which is so simple to grow and oxidise to generate the catalytic surface studied in the present work.

Cu(100) is a cheap face of the compact cubic copper to form. It is moderately reactive as a reducing agent. In the presence of low-pressure air/oxygen, it is partially oxidised. This process was extensively studied in previous work and found to occur at defect sites, even with trace O_2 . [5]. The resulting catalyst selectively oxidises methane to methanol (major product at room temperature and pressure) and further to formaldehyde and finally, formic acid. The activation barrier for the first step has been estimated at 20 kcal/mol. [4].

These partial oxidations never produce CO_2 . They are selective. Under normal conditions, methanol is the only product. The reaction can be stopped at this stage or the methanol used for further mild oxidation, which selectively yields formaldehyde at temperatures above 300K and low pressure (e.g. in a vacuum chamber, as observed in our laboratory). The final product is formadehyde, obtained at atmospheric pressure in the limit of long contact time with the oxidized copper catalyst: it is the product of thermodynamic control.

Formaldehyde is the kinetic control product and its yield is improved by removing the H_2 bi-product. This was simply done with the vacuum pump.

In conclusion, this DFT and Car-Parrinello study confirms the selective oxidation products observed and we suggest a cheap catalytic set-up using partially oxidised Cu(100).

Bibliography

- [1] Electronic Structure: Basic Theory and Practical Methods Richard M. Martin Cambridge University Press, (Vol 1) 2004
- [2] J. P. Perdew and K. Burke and M. Ernzerhof, Phys. Rev. Lett. 77, 3865, (1996).
- [3] R. Car and M. Parrinello, Phys. Rev. Lett, 22, 2471, (1985).
- [4] N. Absi, PhD (2009). Available at www.inist.fr (in French).
- [5] A. Ben Hadj Hamouda, N. Absi, P.E. Hoggan and A. Pimpinelli. Growth instabilities and adsorbed impurities: a case study. Phys Rev B 77(2008) 245430.
- [6] M.J. Lyle, O. Warschkow, B. Delley, C. Stampfl, Surface Science 641 (2015) 97-104
- [7] Z. Jiang, B. Wang, T. Fang, Applied Surface Science 320 (2014) 256-262
- [8] Y. Lou, Q. Tang, H. Wang, B. Chia, Y. Weng, Y. Yang, Applied Catalysis A: General 350 (2008) 118-125
- [9] R. Zhang, T. Duan, L. Ling, B. Wang, Applied Surface Science 341 (2015) 100-108

Theory and simulation of selective hydrocarbon oxidation at copper surfaces: Part II short-chain alkene expoxidation and bi-reactions.

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Abstract: This work continues a series of Density Functional Theory (DFT) studies on mild oxidation by partially oxidised copper. The Cu(100) face has been shown to become a useful selective oxidation catalyst by previous studies of our group.

Previous work by a number of authors, using DFT, highlights partial oxidation, most commonly epoxidation of ethylene to oxirane. This reaction occurs on copper and silver surfaces. Here we demonstrate the usefulness and selectivity of a cheap catalytic system. It comprises partially oxidised Cu(100), synthesized as described in our previous article.

The present study focuses on epoxidation of ethylene and, more unusually propylene. Ethylene epoxidation selectively gives oxirane and that of propylene gives a number of products, initially the epoxide but also acrolein. These reactions are analysed in detail in this work.

The complete oxydation product, CO₂ was absent from these systems.

Introduction.

This work describes mild oxidation of alkenes at copper catalyst surfaces. The oxidation of ethylene to form the epoxide is well-documented on silver surfaces with oxide islands (formally Ag_3O_4 on Ag (100) or even close-packed Ag (111).). The expense of these efficient catalysts has been the driving force for investigating inexpensive alternatives, based on copper. In the literature, there has even been controversy regarding advantages of copper for ethelyne to epoxide selectivity (see Illas and Lambert as compared with Van Santen). This work reports partial oxidation of Cu(100) and its subsequent selective use as a mild oxidation catalyst.

Theory.

The density functional approach (DFT) is used in a plane-wave basis and dynamics carries out at the Car-Parrinello level. A full description of the approach used is given in part I of this two-part contribution (i.e. the previous article in this volume).

Software implementations used

Plane-wave DFT is implemented in a number of software packages. This work uses the freeware ABINIT on a parallel PC cluster.

Results

Two alkenes were oxidised on Cu(100) with a sparce layer of adsorbed atomic oxygen. This is the same oxidation catalyst studied in depth previously in our group [5] and follows the DFT methods used for methane oxidation in Part I of this work, [6].

First, ethylene was adsorbed and efficiently gave the epoxide oxirane. No complete oxidation to CO_2 was observed and our findings correspond to those of [7]. This work finds Cu(111) is more selective than Ag(111). Silver oxides are also efficient for ethylene epoxidation [8].





Oxirane (formation)



Oxirane epoxide (product)

Nevertheless, the industrial silver oxide catalysts (of [8]) are also expensive and here we used a partial oxide of copper (exposing the (100) face). This follows a direct mechanism:



The second alkene studied on Cu(100) was proplylene. It formed an oxide then acrolein (low P).





Initial oxide









Steps towards acrolein

Previously reported studies have acrolein as a product in competition with the epoxide [9]. This work shows that supported copper oxide selectively yields acrolein at low pressure and propylene oxide otherwise. This is summarised in the scheme above.

After initial re-arrangements, the first-formed epoxide from propene is de-hydrogenated by copper to yield acrolein selectively.

Discussion and conclusions.

This work highlights the mild conditions for oxydation provided by partially oxidised Cu(100). For epoxidation, barriers are between 17 and 20 kcal/mol. These catalysts are selective for epoxides and in the case of propylene, the epoxyde may re-adsorb at Cu(100) and be de-hydrogenated to acrolein.

Such selectivity has already been described for supported catalysts in [9]. The present work confirms this step is favored by low pressure (experimental conditions under vacuum pumping) and is similar to the methanol de-hydrogenation yielding formaldehyde in this respect (see [6]).

The key point is that no complete oxidation to CO_2 occurs and that product selectivity generally favors the first-formed (epoxyde) but under specific physico-chemical conditions the other products may be obtained, particularly by de-hydrogenation on the copper.

Bibliography.

- [1] Electronic Structure: Basic Theory and Practical Methods Richard M. Martin Cambridge University Press, (Vol 1) 2004
- [2] J. P. Perdew and K. Burke and M. Ernzerhof, Phys. Rev. Lett. 77, 3865, (1996).
- [3] R. Car and M. Parrinello, Phys. Rev. Lett, 22, 2471, (1985).
- [4] N. Absi, PhD (2009). Available at <u>www.inist.fr</u> (in French).

- [5] A. Ben Hadj Hamouda, N. Absi, P.E. Hoggan and A. Pimpinelli. Growth instabilities and adsorbed impurities: a case study. Phys Rev B 77(2008) 245430.
- [6] N. Absi and P. E. Hoggan. Theory and simulation of selective hydrocarbon oxidation at copper surfaces: Part I methane mild oxidation to methanol, formaldehyde and formic acid. J. Mediter. Chem. (mes2014 issue pp.33-40).
- [7] D. Torres, N. Lopez, F. Illas, and R. M. Lambert J. Am. Chem. Soc. 2005, 127, 10774
- [8] M.O. Ozbek, I. Onal, R.A. van Santen, Journal of Catalysis 284 (2011) 230-235.
- [9] Y. Wang, H. Chu, W. Zhu, and Q. Zhang. Catal. Today, 131 (2008) 496.