

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/244136504>

On the effects of basis-set in studying the hydration and dissociation of HF in cubic HF(H₂O)₇ clusters

ARTICLE *in* CHEMICAL PHYSICS LETTERS · FEBRUARY 2008

Impact Factor: 1.9 · DOI: 10.1016/j.cplett.2008.01.002

CITATIONS

7

READS

15

3 AUTHORS, INCLUDING:



Zhi-Zhong Xie

Wuhan University of Technology

21 PUBLICATIONS 255 CITATIONS

SEE PROFILE



Yew Soon Ong

Nanyang Technological University

197 PUBLICATIONS 4,625 CITATIONS

SEE PROFILE



On the effects of basis-set in studying the hydration and dissociation of HF in cubic $\text{HF}(\text{H}_2\text{O})_7$ clusters

Zhi-Zhong Xie^a, Yew-Soon Ong^a, Jer-Lai Kuo^{b,*}

^a School of Computer Engineering, Nanyang Technological University, 639798 Singapore, Singapore

^b School of Physical and Mathematical Sciences, Nanyang Technological University, 637371 Singapore, Singapore

Received 25 November 2007; in final form 2 January 2008

Available online 8 January 2008

Abstract

We have carried out a systematic study on the performance of Pople-style basis functions on the structure, electronic energies, vibrational spectra of the cubic $\text{HF}(\text{H}_2\text{O})_7$ clusters with B3LYP method. Molecular structure and relative energy among the orientational isomers converge quickly with respect to the basis set and we found that, for most of the purposes, 6-311+G(d,p) represents the most economic choice to yield reliable results. Studies on the potential energy surface for the HF dissociation reactions show that smaller basis set tends to favor fluoric acid dissociation and the barrier height is sensitive to the basis set.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

In contrast to the other three hydrogen halides (HCl, HBr and HI), hydrogen fluoride (HF) is well-known to behave as a weak acid in low concentration – a subject that has been investigated extensively in theory [1–9]. One possible origin of the weak acidity has been customarily attributed to the enhanced F–H bond strength as well as the ability to form a strong hydrogen bond with one water molecule. In addition, the presence of the $\text{F}^- \cdots \text{H}_3\text{O}^+$ ion pair and its unfavorable separation can be ascribed as another alternative explanation for such phenomena [1–3].

The acid dissociation of HF in water clusters has been used as a model system. Re [7] carried out a molecular orbital study on the structures and the relative stability of $\text{HF}(\text{H}_2\text{O})_n$ ($n = 1–7$) at B3LYP/D95++(p,d) level and concluded the most stable structure is found to be the undissociated type (UD) for up to $n = 6$. This conclusion was later confirmed by Kim et al. [10] based on examining a more extensive set of structural isomers using both B3LYP and MP2 and with larger basis sets. Nevertheless, Re also discovered that the contact ion pair (CIP) type of $\text{HF}(\text{H}_2\text{O})_7$

could be more stable than the UD type by 3.3 kcal/mol by comparing two structures constructed by adding one water to the existing $\text{HF}(\text{H}_2\text{O})_6$.

The dissociation of HF with seven water was revisited by Kuo and Klein [11,12]. They examined 39 symmetrically distinct cubic $\text{HF}(\text{H}_2\text{O})_7$ isomers and found self-dissociations to form the zwitter ions (ZW) [12] in the cubic $\text{HF}(\text{H}_2\text{O})_7$ and it was found that ZW structures are energetically comparable to UD structures. It also was noted the relative energetic is sensitive to the basis set and the small basis set (ccpvdZ) used for geometry optimization could have artificially promoted the dissociation. Recently, Kim et al. [13] revisited this issue for the closed structures of $\text{HF}(\text{H}_2\text{O})_{7–10}$ using 6-311++G^{**}(sp). In contrast to Kuo's results, their calculations on $\text{HF}(\text{H}_2\text{O})_7$ show that self-dissociation do not occur and the original UD and CIP structures remain as stable local minima.

The inconsistency of these theoretical studies is likely a result of the different basis sets employed. In this work, taking the cubic $\text{HF}(\text{H}_2\text{O})_7$ as an example, we study how the choice of basis sets influences the structures, relative electronic energies and vibrational spectra of UD, CIP and ZW types' HF-water clusters. In addition, the potential energy surfaces for the dissociation of HF in the mixed-clusters have been investigated in the present work. One

* Corresponding author. Fax: +65 6316 2967.

E-mail address: jlkuo@ntu.edu.sg (J.-L. Kuo).

of our core motivations is to gain a better understanding on the effects and performance of using different basis sets and identify the most economic basis sets for the benefits of future studies on larger mixed HF-water clusters.

2. Computational details

All 39 symmetrical distinct structure of cubic $\text{HF}(\text{H}_2\text{O})_7$ were optimized using B3LYP/6-31+G* and all of them retain as UD or CIP type. The same set of initial structures, when optimized using B3LYP/cc-pvDZ, yield two ZW structures. We have therefore re-optimized the two ZW structures with 6-31+G* and both remain as local minima. The most stable conformation in UD, ZW and CIP shown in Fig. 1 are selected for further investigations.

To gauge the basis set effects and to link up with previous works done on this system, we have chosen a group of Pople-style basis sets ranging from 6-31G(d,p) to 6-311++G(3df,2pd) [14,15] and the 6-311++G(d,p)(sp) basis set used by Kim [10,13] (see Table 1 for details). Electronic energy is recast as the interaction energy ($\Delta E = E_{\text{HF}(\text{H}_2\text{O})_7} - E_{\text{HF}} - 7E_{\text{H}_2\text{O}}$) and the relative stability among the three isomers. Vibration spectra and zero-point energy are obtained by computing the analytical second derivatives under the harmonic approximation.

The transition states for the dissociation of HF have been thoroughly examined with several basis sets selected

from those listed in Table 1. Frequency and IRC [16] calculations were carried out to confirm that these structures are indeed first-order saddle points and relevant to the respective UD and ZWs. All calculations were performed based on the GAUSSIAN 03 software package [17].

3. Results and discussion

3.1. Optimized structures

Since the effects of basis set on the structure of the neutral water clusters have been studied by Lenz and Ojamae [14], we will only focus on selected bond length that are related to HF and the ions in the three lowest-energy isomers see Fig. 1. The calculated bond lengths with ten different basis sets are summarized in Table 1. The first observation is that inclusion of diffuse functions on oxygen atom is important to the bond length. This is evident that the differences between F–O distances obtained by using 6-31G(d,p) and 6-31+G(d,p) in three isomers all exceed 0.02 Å. The diffuse functions adding on hydrogen (++), on the other hand, do not seem to play a significant role.

Secondly, we found that ZW is less sensitive to the basis set, followed by the UD structure and the converged bond lengths can be calculated with 6-311+G(d,p). The only exception is the F–H in CIP which requires additional polarizable functions. The F–H in CIP shrunk by 0.03 Å when 6-311+G(2d,2p) is used. We should note here that this small shrinkage in F–H is associated with 100 cm^{-1} red-shift in vibrational frequency – which will be discussed latter.

Based on the above considerations, we conclude that 6-311+G(d,p) yields sufficient accuracy for molecular geometry. Beyond this basis set, additional diffuse and polarization functions are not important for the bond distances (with the exception of the F–H in the CIP).

3.2. Electronic energy

The Electronic energies are presented as the interaction energy and relative energies. The latter, summarized in Table 2, shows the relative stability among ZW, CIP,

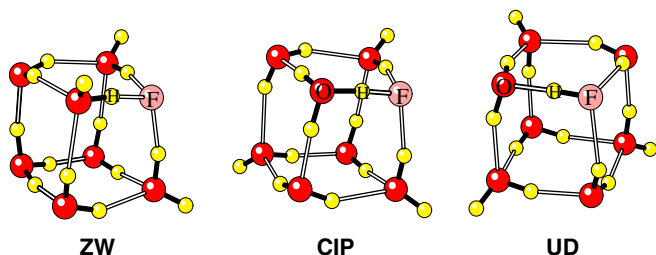


Fig. 1. The most stable zwitterionic (ZW), contact ion pair (CIP) and undissociated (UD) structures of cubic $\text{HF}(\text{H}_2\text{O})_7$.

Table 1
The selected bond lengths (see Fig. 1 for definition) calculated using B3LYP method with different basis sets

Methods	ZW			CIP		UD	
	F–O	F–O	F–H	F–O	F–H	F–O	F–H
B3LYP/6-31G(d,p)	2.492	2.392	1.321	2.405	1.029	2.405	1.029
B3LYP/6-31+G(d,p)	2.521	2.375	1.282	2.426	1.017	2.426	1.017
B3LYP/6-31++G(d,p)	2.519	2.376	1.282	2.427	1.016	2.427	1.016
B3LYP/6-311+G(d,p)	2.526	2.351	1.210	2.450	0.999	2.450	0.999
B3LYP/6-311++G(d,p)	2.527	2.352	1.218	2.445	0.999	2.445	0.999
B3LYP/6-311++G(d,p)(sp)	2.527	2.352	1.218	2.445	0.999	2.445	0.999
B3LYP/6-311+G(2d,2p)	2.527	2.349	1.186	2.445	1.000	2.445	1.000
B3LYP/6-311++G(2d,2p)	2.527	2.348	1.184	2.445	1.000	2.445	1.000
B3LYP/6-311++G(2df,2pd)	2.520	2.351	1.182	2.446	0.999	2.446	0.999
B3LYP/6-311++G(3df,2pd)	2.522	2.349	1.182	2.444	1.000	2.444	1.000
MP2/aug-cc-pvdz	2.521	2.366	1.250	2.461	0.996	2.461	0.996

The unit is in Å.

Table 2
The relative energies in kcal/mol are calculated at different levels

Methods	ZW	CIP	UD
B3LYP/6-31G(d,p)	1.1(1.1)	0.0(0.0)	0.2(0.4)
B3LYP/6-31+G(d,p)	2.2(2.6)	0.6(0.6)	0.0(0.2)
B3LYP/6-31++G(d,p)	2.1(2.5)	0.6(0.5)	0.0(0.1)
B3LYP/6-311+G(d,p)	3.5(4.0)	1.4(0.8)	0.0(0.1)
B3LYP/6-311++G(d,p)	3.4(3.9)	1.4(0.8)	0.0(0.1)
B3LYP/6-311++G(d,p)(sp)	3.5(4.1)	1.3(0.8)	0.0(0.1)
B3LYP/6-311+G(2d,2p)	3.5(4.0)	1.2(0.4)	0.0(0.1)
B3LYP/6-311++G(2d,2p)	3.4(3.9)	1.1(0.3)	0.0(0.1)
B3LYP/6-311++G(2df,2pd)	3.6(4.1)	1.3(0.5)	0.0(0.2)
B3LYP/6-311++G(3df,2pd)	3.7(4.1)	1.2(0.5)	0.0(0.0)
MP2/aug-cc-pvdz	3.2(3.7)	1.1(0.8)	0.0(0.0)

The values in parenthesis are after zero point energy correction.

and **UD** at different levels. We found that it is fairly easier to catch the qualitative trend, the ordering of the relative stability among the three isomers is correct even with a moderate basis set (6-31+G(d,p)). But to reduce the effects of basis sets and get quantitatively accurate result, we found that the triple-zeta basis set is required. Among the basis sets we tested, 6-311+G(d,p) yield sufficiently accurate relative energies. Adding more diffusion functions on the H atoms and polarizable functions makes insignificant changes (less than 0.2 kcal/mol).

In Table 2, we also present the relative stability of the three isomers at MP2/aug-cc-pvdz level. The relative energies are 3.3, 1.1 and 0.0 kcal/mol for **ZW**, **CIP**, and **UD**, respectively. They are comparable with the values calculated at B3LYP level theory with triple-zeta basis sets. In short, **UD** is more stable than **CIP** but when the zero point energy (ZPE) correction is included, the energy difference between **UD** and **CIP** decreases to less 1.0 kcal/mol.

The electronic interaction energies, $\Delta E = E_{\text{HF}(\text{H}_2\text{O})_7} - E_{\text{HF}} - 7E_{\text{H}_2\text{O}}$, are compiled in Table 3. It is noted that the inclusion of diffuse functions in the heavy atoms basis (+) significantly reduces the magnitudes of interaction energies, while the diffuse functions on hydrogen play minor roles. Adding diffuse functions on heavy atoms is much more important than to enlarge the basis set from the double-zeta to triple-zeta. With the increasing of basis sets, the interaction energies of these three clusters decrease incrementally. The variation of the interaction energies is about 2 kcal/mol when basis function increases from 6-311+G(2d,2p) to 6-311++G(3df,2pd), therefore we do not expect that our calculated interaction is approaching the complete basis set limit. Furthermore, if MP2/aug-cc-pvdz calculations were used as the benchmark, the 6-311+G(d,p) is recommended for calculating the electronic energies.

Zero point energy (ZPE) has a more profound influence in determining the interaction energy than relative energy. By comparing the interaction energy with/without ZPE (interaction energies with ZPE correction are given in parentheses), it is clear that without ZPE the interaction is off by 20 kcal/mol. It is also worth to noting that the

ZPE contribution converges faster than the contribution from electronic energy; therefore it is justified to use a smaller basis for calculating ZPE in determining the interaction energy.

In summary, we found that the interaction energies converge much slower than relative stability. Even with 6-311++G(3df,2pd), we cannot obtain a converged interaction energy. Accurate relative stability, on the other hand, can be obtained with moderate basis set and we found that 6-311+G(d,p) is sufficient. It should be noted that when a larger set of isomers including non-cubic structures is considered in the comparison, this conclusion may be slightly altered due to unbalance of magnitudes of BSSE between the most compact cubic structures and less compacted non-cubic structures.

3.3. IR spectra

The IR spectra for **ZW**, **CIP**, and **UD** calculated at B3LYP level are depicted in Fig. 2. The spectra for **ZW** are least sensitive to the basis sets. The two asymmetric stretching of the H_3O^+ peaks are located at $\sim 2500\text{ cm}^{-1}$ high-lighted in Fig. 2a and the frequencies are slightly blue-shifted with larger basis set.

In the range of $1000\text{--}2000\text{ cm}^{-1}$, most of the peaks for the spectra of **CIP** are not sensitive to basis sets. The vibration mode associated with the motion of the shared proton in the contact ion pair is highlighted in Fig. 2b. When the triple-zeta basis set, 6-311+G(d,p), is used, the frequency of the share proton motion is blue shifted to around 1300 cm^{-1} and there is little change between 6-311+G(d,p) and 6-311++G(d,p)(sp). Additional polarizable functions seem to further red-shift the peak position to around 1200 cm^{-1} . In comparison with the difference calculated between triple-zeta and double-zeta basis sets ($>500\text{ cm}^{-1}$), 100 cm^{-1} red shift is not very significant. We should also note that the basis set dependence of this vibrational frequency is in line with the basis set dependence of the R(F–H) length in **CIP** (see Table 1).

The dependence of the IR spectra of **UD** on the basis set is very similar to that of the **ZW**. The only notable change

Table 3
Interaction energies in kcal/mol for $\text{HF}(\text{H}_2\text{O})_7$

Methods	ZW	CIP	UD
B3LYP/6-31G(d,p)	–116.7(–139.0)	–117.8(–141.0)	–117.6(–141.4)
B3LYP/6-31+G(d,p)	–82.0(–60.7)	–83.6(–62.7)	–84.2(–63.2)
B3LYP/6-31++G(d,p)	–82.0(–60.7)	–83.6(–62.7)	–84.2(–63.2)
B3LYP/6-311+G(d,p)	–77.1(–56.1)	–79.2(–59.2)	–80.6(–59.9)
B3LYP/6-311++G(d,p)	–77.1(–56.1)	–79.2(–59.3)	–80.6(–60.0)
B3LYP/6-311++G(d,p)(sp)	–77.1(–56.0)	–79.2(–59.2)	–80.6(–60.0)
B3LYP/6-311+G(2d,2p)	–70.5(–50.1)	–72.8(–53.7)	–74.0(–54.0)
B3LYP/6-311++G(2d,2p)	–70.6(–50.2)	–72.9(–53.8)	–74.0(–54.1)
B3LYP/6-311++G(2df,2pd)	–69.3(–49.2)	–71.7(–52.9)	–73.0(–53.2)
B3LYP/6-311++G(3df,2dp)	–68.7(–48.6)	–71.2(–52.3)	–72.4(–52.5)
MP2/aug-cc-pvdz	–76.5(–56.0)	–78.6(–58.9)	–79.7(–59.6)

The values in parentheses are after zero point energy correction.

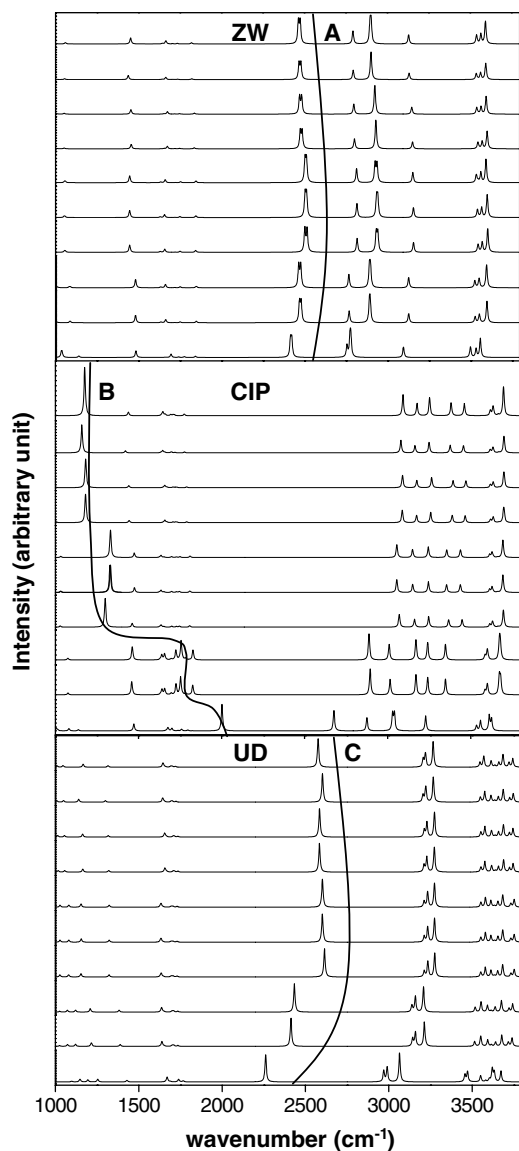


Fig. 2. IR spectra of the ZW, CIP and UD structures calculated using B3LYP method with different basis sets. The basis sets go from 6-31G(d,p) (bottom) to 6-311++G(3df,2pd) (top). A few vibrational modes associated with the motion of HF and H_3O^+ are highlighted: (A): the O–H stretching of H_3O^+ in ZW; (B): the F–H stretching in CIP; (C) the F–H stretching in UD.

is the HF stretching and even that the frequency is stabilized at about 2600 cm^{-1} at 6-311+G(d,p), and extension of any additional diffusion/polarizable functions have little effects.

3.4. Proton transfer reaction

Two ZW conformers were located starting from the 39 cubic-HF(H_2O)₇ at B3LYP/cc-pvdz level, which are labeled as ZW1 (equivalent to ZW in Fig. 1) and ZW2. The corresponding undissociation conformers are denoted as UD1 and UD2, respectively. The four conformers are reoptimized at B3LYP level theory with the 6-31+G(d,p),

6-311+G(d,p) and 6-311+G(2d,2p) basis sets. Unlike at B3LYP/cc-pvdz level, the self-dissociation phenomena could not be found for UD1 and UD2 and both of them are local minima when diffuse functions are involved in the basis sets. This is a clear indication that the dissociation process is very sensitive to the basis set.

The two transition states for the dissociation reactions from UD1 to ZW1 and UD2 to ZW2 are located, which are denoted as TS1 and TS2 in Fig. 3, respectively. The energy profile for the HF dissociations, as shown in Fig. 3, have similar dependence on the basis set. The barrier heights calculated with triple-zeta basis (6-311+G(d,p)) sets are higher than those calculated by using the double-zeta basis set (6-31+G(d,p)) and the slight energy differences between the two triple-zeta basis sets (6-311+G(d,p) and 6-311+G(2d,2p)) indicates the insignificance of that additional polarization functions for triplet-zeta basis sets. It is clear that the smaller basis set is in favor of the HF dissociation because the barrier heights calculated at B3LYP/6-31+G(d,p) level are about 1 kcal/mol lower than those calculated with larger basis sets for TS1 and TS2.

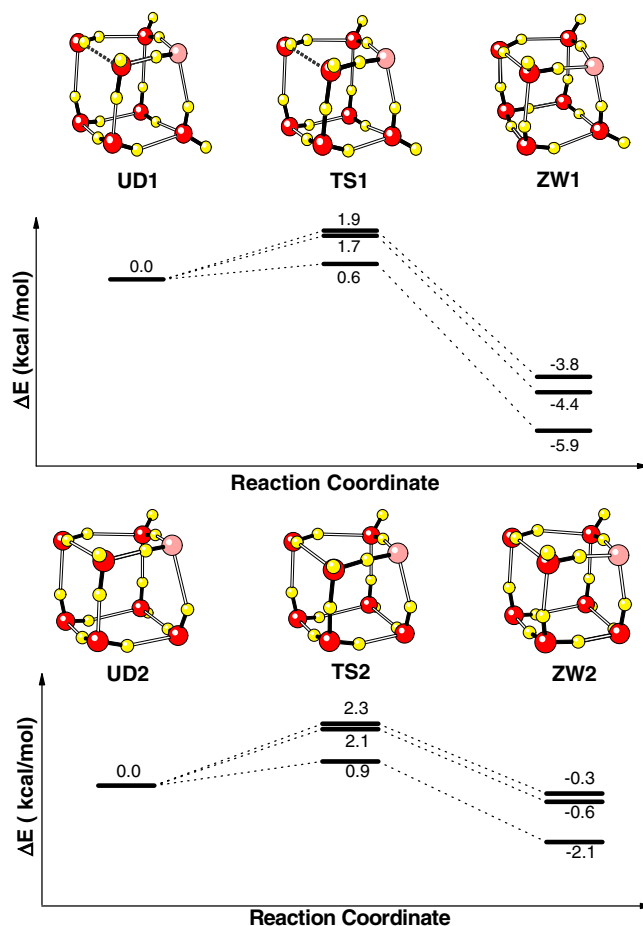


Fig. 3. The potential energy surfaces (in kcal/mol) for the proton transfer reactions calculated with three different basis sets. From bottom to top, the basis sets range in the increasing order of 6-31+G(d,p), 6-311+G(d,p) and 6-311+G(2d,2p).

4. Conclusion

In the present work, a comprehensive investigation on the convergence of basis sets to predict the structure, electronic energies, IR spectra and the PES for the HF dissociation is reported. For structures optimization and relative energy, 6-311+G(d,p) seems to be the most economic choice to yield reasonably accurate geometry. For the IR spectra of **UD** and **ZW**, 6-311+G(d,p) is also sufficient to yield consistent peak positions. The IR spectra of **CIP** isomer are more sensitive to basis sets than those of **UD** and **ZW**. For the dissociation of HF into zwitterionic clusters, the inclusion of diffuse functions is crucial to get even a qualitative description on the transition states. Furthermore, the relative barrier heights display a systematic trend that smaller basis sets tend to favor the dissociation of fluoric acid.

Acknowledgements

This work was supported in part under URC Grant RG34/05, RG35/05, RG57/05, and RG170/06 from Nanyang Technological University and the A*STAR SERC Grant No. 052 015 0024 administered through the National Grid Office. Computational resource, in part, pro-

vided by Computational Chemistry Lab at Nanyang Technological University is greatly appreciated.

References

- [1] E.M. Cabaleiro-Lago, J.M. Hermida-Ramon, J. Rodriguez-Otero, J. Chem. Phys. 117 (2002) 3160.
- [2] S.Y. Re, Y. Osamura, Y. Suzuki, H.F. Schaefer, J. Chem. Phys. 109 (1998) 973.
- [3] M.E. Alikhani, B. Silvi, J. Mol. Struct. 706 (2004) 3.
- [4] K. Ando, J.T. Hynes, Faraday Dis. (1995) 435.
- [5] K. Ando, J.T. Hynes, J. Phys. Chem. A 103 (1999) 10398.
- [6] S. Raugei, M.L. Klein, J. Am. Chem. Soc. 125 (2003) 8992.
- [7] S.Y. Re, J. Phys. Chem. A 105 (2001) 9725.
- [8] A.J. Sillanpaa, C. Simon, M.L. Klein, K. Laasonen, J. Phys. Chem. B 106 (2002) 11315.
- [9] C. Simon, M.L. Klein, Chemphyschem 6 (2005) 148.
- [10] S. Odde, B.J. Mhin, S. Lee, H.M. Lee, K.S. Kim, J. Chem. Phys. 120 (2004) 9524.
- [11] J.L. Kuo, J.V. Coe, S.J. Singer, Y.B. Band, L. Ojamae, J. Chem. Phys. 114 (2001) 2527.
- [12] J.L. Kuo, M.L. Klein, J. Chem. Phys. 120 (2004) 4690.
- [13] S. Odde, B.J. Mhin, K.H. Lee, H.M. Lee, P. Tarakeshwar, K.S. Kim, J. Phys. Chem. A 110 (2006) 7918.
- [14] A. Lenz, L. Ojamae, Chem. Phys. Lett. 418 (2006) 361.
- [15] M.C.W. Holthausen, A Chemist's Guide to Density Theory. Second Edition (2001) 217.
- [16] K. Fukui, Acc. Chem. Res. 14 (1981) 363.
- [17] M. J. Frisch et al., Gaussian Inc., Wallingford, CT 2004.