

## Structural, vibrational and electronic properties of small group IV oxide clusters in lower and higher spin state: a DFT study

Neeraj Misra\*, Apoorva Dwivedi, and Anoop Kumar Pandey

*Department of Physics, Lucknow University, Lucknow 226007, India*

Received 25 May 2011; Accepted (in revised version) 4 July 2011

Published Online 18 February 2012

---

**Abstract.** Structural, vibrational and electronic properties of the zirconium oxide clusters [ $n=1-6$ ] are calculated to investigate the changes in, lower and higher state by Density functional theory with the B3LYP exchange-correlation functional using LANL2DZ as the basis set. We optimize several isomers for each size in order to obtain the lowest energy structures and to understand the growth behavior. In the next step, these optimized geometries are used to calculate the binding energy and HOMO-LUMO gap (band gap) of the clusters. In all cases ring type structures are found to be most favorable but for  $n=3-6$ , the ring structures are not planar suggesting that the bonding nature in these cluster has some covalent character.

**PACS:** 31.15.A, 31.15.es, 31.15.V

**Key words:** density functional theory, zirconium oxide clusters, HOMO-LUMO

---

## 1 Introduction

In the past two decades small and medium sized semiconductor clusters have been extensively studied due to their extremely important role in the physical and chemical processes taking place at the metal-semiconductor interface [1–5]. Zirconia assumes importance because of its high melting point, low thermal conduction and high ionic conductivity. The cubic phase of zirconia also has a very low thermal conductivity, which has led to its use as a thermal barrier coating or TBC in jet and diesel engines to allow operation at higher temperatures. A great deal of research is being carried out to improve the quality and durability of these coatings. It is used as a refractory material, in insulation, abrasives, enamels and ceramic glazes. Stabilized zirconia is used in oxygen sensors and fuel cell membranes because it has the ability to allow oxygen ions to move freely through the crystal structure at high temperatures. This high

---

\*Corresponding author. *Email address:* neerajmisra11@gmail.com (N. Misra)

ionic conductivity (and a low electronic conductivity) makes it one of the most useful electroceramics. Zirconia is also an important high- $k$  dielectric material that is being investigated for potential applications as an insulator in transistors in future nanoelectronic devices [6]. Its durability permits its use as a container for the safe disposal of high-level nuclear waste [7]. Small clusters of zirconium oxide can be taken as model geometries /models to understand the basic physics and chemistry of structures at nanolevel. Since the nanoclusters can be seen as intermediate between single atom/molecule and bulk materials the physical properties of material are dimension dependent and hence are scalable with respect to the amount of atoms in the material so effectively, that at nanoscale these properties vary with every change in the number of atoms.

Therefore, the studies on ZrO and its clusters assumes importance and in this communication we investigate the electronic, structural and vibrational properties of ZrO clusters with an increase in size in lower and higher state both. From the applications point of view, it shall be fully justified if we try to know the competing isomers as well as their properties such as the stability, HOMO-LUMO gaps, bonding nature etc.

## 2 Computational methods

The theoretical methods used in this study were based on the density functional theory [8] using the three-parameter hybrid functional B3LYP [9, 10] and LANL2DZ [11] as the basis set. The standard LanL2DZ basis as effective core potential with no symmetry constraint is employed here. This basis set provides an effective way to solve two-electron integrals even in case of heavy elements. The previous calculations as revealed in the literature [12–15] have shown that LanL2DZ basis sets of the effective core potential theory were found to be reliable for the geometries, stabilities, and electronic properties of transition metal clusters. The vibrational frequencies under the harmonic approximation, with analytical force constants were calculated. Harmonic vibrational analysis was performed for each system not only to obtain the vibrational frequencies, but also to characterize the nature of the structure obtained in the potential energy surface (PES). All calculations were performed using the Gaussian 09 software package [16].

## 3 Results and discussion

The optimized structures of different isomers are shown in Fig. 1. Isomers marked with 'a' are in lower state and those marked 'b' are in higher state. The details of the structures and the properties of the most stable isomers are given in Tables 1 and 2 for the lower and the higher states. The binding energy per ZrO molecule is calculated from the following equation

$$E_B = \frac{nE_{Zr} + nE_O - E_{ZrO}^n}{n},$$

where  $n$  is the number of ZrO molecules in the cluster. The variation of binding energies and HOMO-LUMO gap of the most favourable structures are shown in Figs. 2 and 3 for the lower

Table 1: Structures, bond lengths (Å), O–Zr–O angle, binding energy per ZrO molecule,  $E_B$  (eV) and HOMO-LUMO gap for  $(ZrO)_n$  clusters,  $n = 1-6$ .

Structure	Bond length (ZrO) Å	Bond angle (O–Zr–O) <sup>o</sup> [in degree]	$E_B$ (eV)	Band gap (eV)
Linear	1.75	–	10.68	1.26
Rhombus	2.03	89.98	13.23	1.43
Pyramidal	1.97	101.76	13.41	1.12
Rhombohedral	1.97–2.35	99.54	13.63	0.75
Capped Distorted Rhombohedron	1.95–2.85	165.96	14.37	1.01
Double Ring	1.97–3.36	83.95–145.02	14.70	0.91

Table 2: Structures, bond lengths (Å), O–Zr–O angle, binding energy per ZrO molecule,  $E_B$  (eV) and HOMO-LUMO gap for  $(ZrO)_n$  clusters,  $n = 1-6$  in higher spin state.

Structure	Bond length (ZrO) Å	Bond angle (O–Zr–O) <sup>o</sup> [in degree]	$E_B$ (eV)	Band gap (eV)
Linear	1.74	–	10.21	$\alpha=2.45$ $\beta=6.09$
Rhombus	1.99	87	31.72	$\alpha=1.18$ $\beta=2.14$
Pyramidal	1.98	88	53.04	$\alpha=2.24$ $\beta=1.69$
Rhombohedral	2.00	95	73.61	$\alpha=1.50$ $\beta=1.66$
Bi pyramidal	2.05	130	118.86	$\alpha=1.00$
Double Ring	1.98	142	119.35	$\alpha=1.95$ $\beta=1.80$

state. The variation of binding energy (BE) and HOMO-LUMO with per ZrO for the higher state is shown in Figs. 4 and 5. Binding energy curves shows the same trend in both the states.

### 3.1 Structure and properties

ZrO molecule has a bond length of 1.75 Å and a quite low binding energy along with a higher HOMO-LUMO gap (Table 1). This suggests that this cluster might exhibit a good dielectric behavior. In ZrO, due to the loss of an electron from the d orbital there is a change in its bond length and binding energy lies between that of neutral and cationic form i.e., 1.19 eV. The bond length is elongated to 2.03 Å in the most favorable isomer (2a in Fig. 1) of  $Zr_2O_2$  which is a rhombus. The binding energy too increases significantly, though these values are still much smaller than for larger clusters.

In Fig. 1, the structures 2 and 2b are taken as initial geometries but it eventually converges to the structure 2a. The O–Zr–O angle in this isomer is much smaller than what is found in the

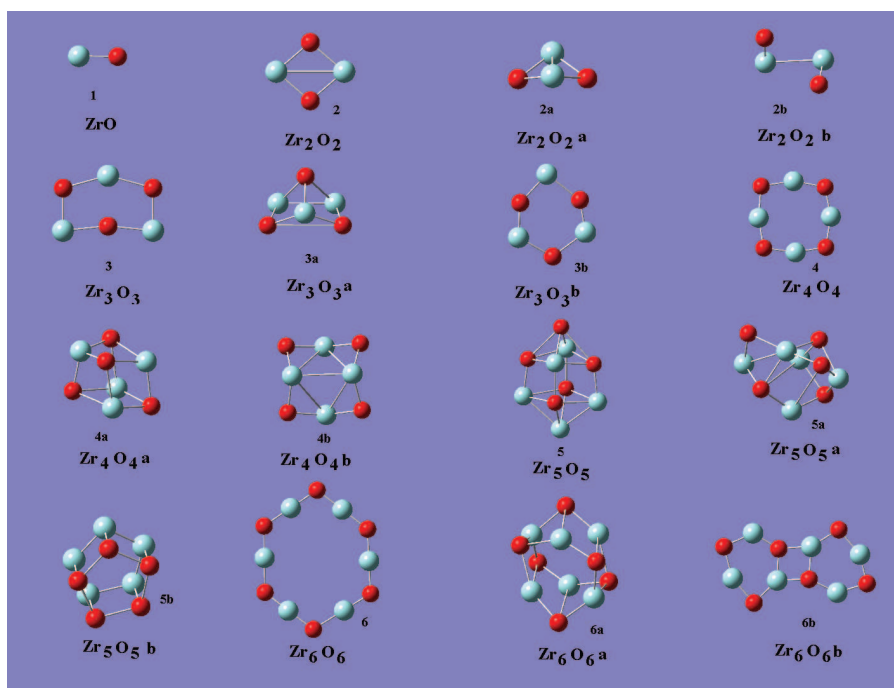


Figure 1: Different structures of  $(\text{ZrO})_n$  molecule.

most favorable structure of larger clusters. In  $\text{Zr}_2\text{O}_2$  neither linear nor rhombic structures are stable but the rhombic structure had the lowest energy having one imaginary frequency. This is due to the out of the plane displacement of oxygen atom.

In order to find a stable dimer the oxygen atom was allowed to bend more (by an angle equal to  $-49^\circ$ ) during geometry optimization and consequently an isomer with no imaginary frequency was found. The electron in the cationic state came from HOMO of oxygen atom and goes to the LUMO of Zr atom. The Zr–Zr bond gets enlarged and to attain stability, the oxygen atom goes out of plane. An interesting feature here is, that in the cationic state there are two types of band gaps and hence ZrO cluster shows an indirect semiconductor behaviour. There is an increase in the binding energy in case of dimer as compared to the monomer and in cationic case this increases abruptly. This strange or rather unusual stability of cationic state of  $\text{Zr}_2\text{O}_2$  can be exploited to find a temperature resistive device.

After trying 3 and 3b as the initial structures, the ring type structure opened up and finally converged to the structure 3a. The Zr–O bond length in this case is shorter as compared to  $\text{Zr}_2\text{O}_2$  cluster and O–Zr–O angle is much larger as shown in Table 1. This may be due to the release of strain in this structure in comparison to the rhombic structure of  $\text{Zr}_2\text{O}_2$ . Consequently, the  $\text{Zr}_3\text{O}_3$  structure becomes more stable. This is also clear from the significant increase in the binding energy of  $\text{Zr}_2\text{O}_2$ .

In  $\text{Zr}_3\text{O}_3$ , due to the loss of an electron, no significant change is observed in the structure

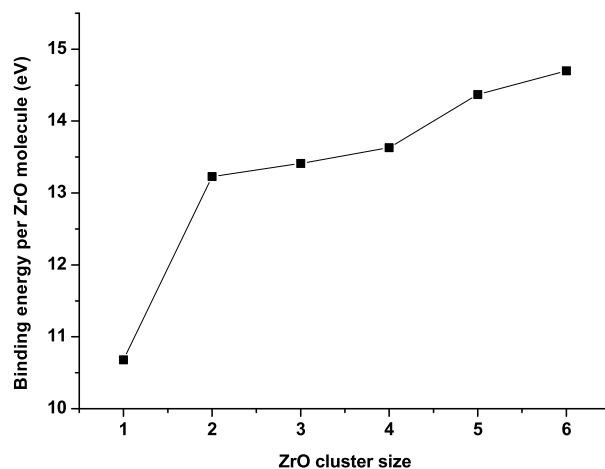


Figure 2: Binding energy per ZrO molecule for the most stable ZrO clusters.

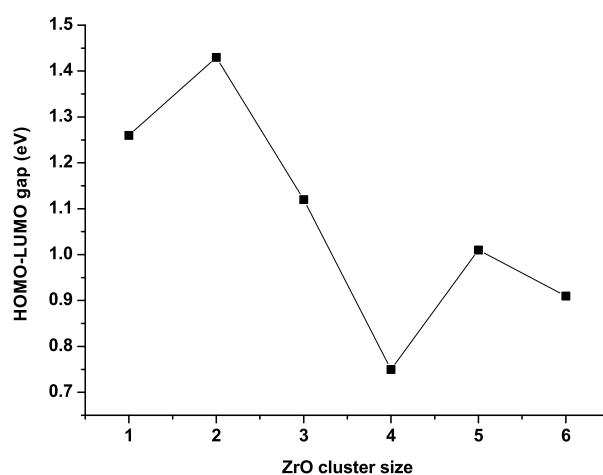


Figure 3: HOMO-LUMO gaps for the most stable ZrO clusters.

except the oxygen atom (centered) moves downward and hence the bond length between oxygen and zirconium atom increases. From the HOMO-LUMO picture it is also clear that in cationic state the electron comes from HOMO of oxygen atom and hence the bond length increases. So, to achieve a stable configuration it shifts downwards and thereby disturbs some bonds. All the features are similar to the dimer except the band gap decrease in case of neutral trimer as compared to the dimer and beta type band gap decrease in cationic case makes it

less reactive.

Out of all the  $Zr_4O_4$  structures, the rhombohedral structure of  $Zr_4O_4$  (4a) shown in Fig. 1 is significantly more favorable due to its lowest energy. Here, it is important to note that in comparison with  $Zr_3O_3$ , the bond length and binding energy of the rhombohedral structure (4a) is more than that of  $Zr_3O_3$  but the value of the HOMO-LUMO gap decreases. The rhombohedral structure (4a) has a higher BE and HOMO-LUMO gap than the unfavorable planar

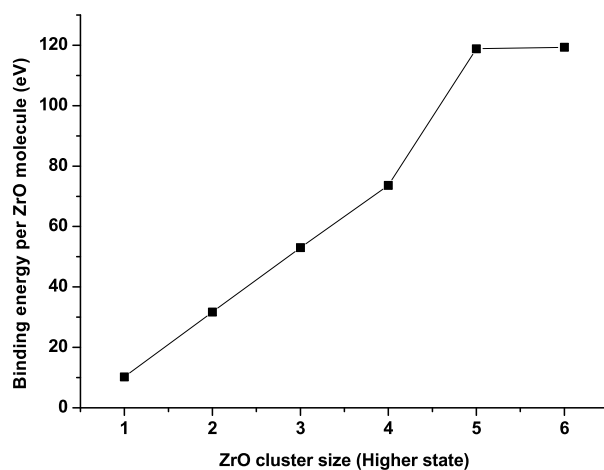


Figure 4: Binding energy for the most stable ZrO clusters in higher state.

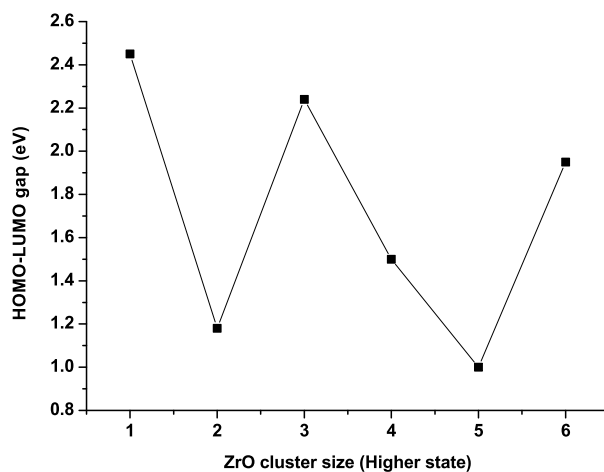


Figure 5: HOMO-LUMO gaps for the most stable ZrO clusters in higher state.

ring structure. In  $Zr_4O_4$  there is no change in the structure but a slight increase in bond length due to the loss of an electron.

In case of  $Zr_5O_5$  we get two optimized structures (5 and 5a) but the capped distorted rhombohedral structure  $Zr_5O_5$  (5a) as shown in Fig. 1 is significantly more favorable due to lower energy as can be seen in Table 1. The capped distorted rhombohedron structure has a significantly higher binding energy than the 3 dimensional structure shown in 5. The O–Zr–O angle in the capped distorted rhombohedron isomer also tends to become close to  $180^\circ$ , thereby imparting more stability. The bond length in isomer (5a) is almost similar to the bond length in isomer 4a but the O–Zr–O angle increases. The difference between the HOMO-LUMO gaps of 5a and 5 is still very large, thus making 5a more favorable than the 5b isomer. In  $Zr_5O_5$ , due to the loss of an electron from neutral to cationic state the structure changes from 5a (distorted) to 5 (bipyramidal) due to rearrangement of atoms. In case of pentamer it acts as a direct semi conductor in both cationic and neutral states with nearly same band gap.

The optimized structure of  $Zr_6O_6$  is shown in Fig. 1(6a). The double ring type structure shown in 6a has the highest BE. Here, it is worth mentioning to note that both zirconium as well as oxygen atoms shift away from the plane. The bond length in 6a is almost similar to the bond length of isomer 5a, but the bond angle O–Zr–O reduces slightly from the values in isomer 5a, with the values ranging between  $83.95^\circ$ – $145.02^\circ$ . The binding energies of the isomers 6 and 6a are considerably lower than the binding energy of 6a and also have very low values of HOMO-LUMO gaps. Therefore, they are much less stable and unfavorable too. In  $Zr_6O_6$ , there is no change in the structure except for a slight change in the bond length due to loss of an electron. Here only the structural changes are being discussed in both the states. In case of hexamer the difference in reactivity becomes large in neutral and cationic cases.

The HOMO-LUMO gap for  $n \geq 3$  is nearly the same with a value close to 1 eV. A HOMO-LUMO plot has also been drawn to exhibit the trend which is almost similar to ZrO clusters.

### 3.2 Vibrational modes analysis

It is clearly evident from the optimized structures of different isomers as shown in Fig. 1. that there are no imaginary frequencies in the most stable structures. For ZrO molecule, the vibrational frequency is  $983 \text{ cm}^{-1}$ . In Fig. 4, the lowest trace spectrum measured for ZrO consists of a broad feature around  $640 \text{ cm}^{-1}$  [17]. ZrO has a known vibrational frequency of about  $900 \text{ cm}^{-1}$  [18] which matches well with the calculated frequency. The FTIR spectra of ZrO is given in Fig. 7. All the frequencies of different structures are given in Table 3. To analyze the calculated frequencies of dimers, the atomic coordinates of  $TM_2X_2$  were chosen in such way that the cluster lie on the  $yz$  plane with the X atoms located along the  $y$ -axis and the TM atoms along the  $z$ -axis. In dimers, the analysis of normal modes reveals that the lowest frequency  $B_{3u}$  corresponds to the out of plane bending, and the highest frequency  $A_g$  involves mainly the vibration of X–X bond, with frequency values somewhat smaller than the corresponding values in  $X_2$  molecules. This is due to the fact that the X–X bond vibration is slightly coupled with the vibration of the TM–X bonds.

Table 3: Vibrational frequencies of different  $(\text{ZrO})_n$  most stable structures in lower state and higher state.

Nanoclusters	Properties	Values ( $\text{cm}^{-1}$ )
ZrO	Frequencies (IR intensity)	983 (127.99) Lower state 990 (101.92) Higher state
Zr <sub>2</sub> O <sub>2</sub>	Frequencies (Mode)	148 ( $B_{3u}$ ), 270 ( $B_{2u}$ ), 276 ( $B_{3g}$ ), 374 ( $A_g$ ), 641 ( $B_{1u}$ ), 667 ( $A_g$ ) Lower state 159 ( $B_{3u}$ ), 270 ( $B_{2u}$ ), 315 ( $B_{3g}$ ), 329 ( $A_g$ ), 676 ( $B_{1u}$ ), 713 ( $A_g$ ) Higher State
Zr <sub>3</sub> O <sub>3</sub>	Frequencies	71, 175, 178, 233, 245, 307, 324, 422, 511, 554, 641, 659 Lower state
Zr <sub>4</sub> O <sub>4</sub>	Frequencies	91, 139, 142, 177, 178, 194, 256, 258, 265, 266, 303, 307, 332, 401, 571, 611, 613, 642 Lower state
Zr <sub>5</sub> O <sub>5</sub>	Frequencies	119, 125, 149, 167, 174, 188, 203, 223, 235, 250, 283, 291, 311, 330, 386, 424, 437, 474, 484, 544, 549, 558, 656, 673 Lower state
Zr <sub>6</sub> O <sub>6</sub>	Frequencies	65, 84, 104, 110, 115, 133, 145, 154, 162, 176, 202, 210, 215, 236, 261, 272, 322, 339, 394, 428, 459, 462, 471, 487, 545, 547, 619, 621, 628, 631 Lower state

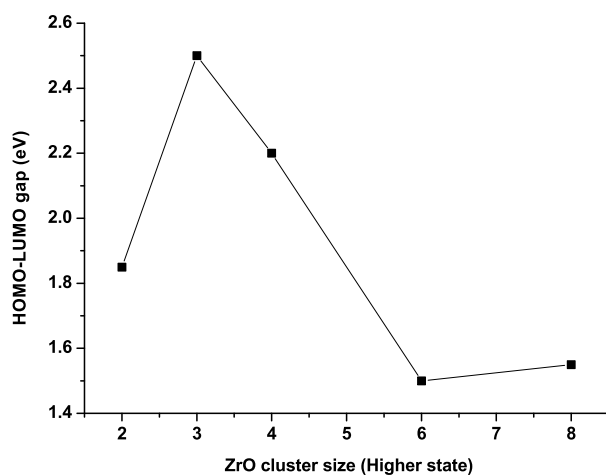


Figure 6: HOMO-LUMO gaps for the most stable O clusters.

## 4 Conclusions

We have studied (both lower and higher state) the structures and properties of small zirconium oxide clusters using ab initio (DFT) calculations. Our results show that there is a difference in the bonding nature of clusters of ZrO compound semiconductors. Our results are also indicative of an increasing trend for the relative preference for 3-dimensional struc-



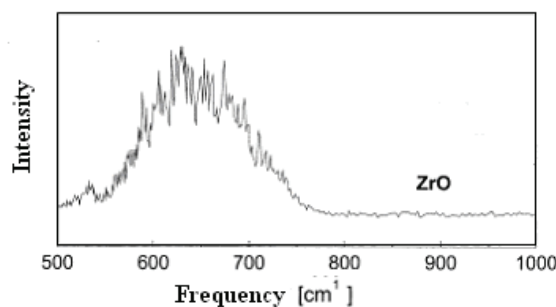


Figure 7: FTIR spectra of ZrO molecule.

tures with an increase in size. The HOMO-LUMO gap for  $n = 1$  and 2 is significantly higher than the other clusters which is a general behavior in elemental semiconductors. Calculated IR spectra shows characteristic IR active modes between 900 and 1000  $\text{cm}^{-1}$  that correspond to Zr–O stretching of isolated oxygen atoms. The most stable isomers contain Zr–O–Zr–O four membered rings that are typical for the bulk structure. For small clusters, motion in these rings gives rise to characteristic IR active modes between 600 and 700  $\text{cm}^{-1}$ .

We prefer the cationic form for the higher order of this cluster and it shows that if we work at the lower order of the cationic cluster the conductivity of such type of cluster is found to be less and can be used as a good dielectric material. In the case of higher state the cluster stability increases so these types of cationic clusters are used in temperature resistive devices. Another striking feature of this study is that the ZrO cluster acts as both direct and indirect semiconductor in different ionic states. This can prove to be very useful as far as industrial application is concerned.

**Acknowledgments.** The corresponding author (NM) is grateful to the University Grants Commission, New Delhi for providing financial assistance.

## References

- [1] S. Li, R. J. Van Zee, W. Jr. Weltner, and K. Raghavachari, Chem. Phys. Lett. 243 (1995) 275.
- [2] E. Kaxiras and K. Jackson, Phys. Rev. Lett. 71 (1993) 727.
- [3] U. Rothlisberge, W. Andreoni, and M. Parrinello, Phys. Rev. Lett. 72 (1994) 665.
- [4] K.-M. Ho, A. A. Shvartsburg, B. Pan, Z.-Y. Lu, C.-Z. Wang, J. G. Wacker, J. Fye, and M. F. Jarrold, Nature (London) 392 (1998) 582.
- [5] I. Rata, A. A. Shvartsburg, M. Horoi, T. Frauenheim, K. W. Michael Siu, and K. A. Jackson, Phys. Rev. Lett. 85 (2000) 546.
- [6] Zirconium dioxide, Wikipedia, free encyclopedia, March 2010.
- [7] G. R. Lumpkin, J. Nucl. Mater. 274 (1999) 206.
- [8] P. Hohenberg and W. Kohn, Phys. Rev. 136 (1964) B864.
- [9] A. D. Becke, J. Chem. Phys. 98 (1993) 5648.
- [10] C. Lee, W. Yang, and R. G. Parr, Phys. Rev. B 37 (1988) 785.
- [11] J. P. Hay and R. W. Wadt, J. Chem. Phys. 82 (1985) 270.

- [12] J. Wang and J.G. Han, J. Chem. Phys. 123 (2005) 064306.
- [13] J. G. Han and F. Hagelberg, J. Mol. Struct. (Theochem.) 549 (2001) 165.
- [14] P. Guo, Z. Y. Ren, F. Wang, J. Bian, J. G. Han, and G. H. Wang, J. Chem. Phys. 121 (2004) 12265.
- [15] L. J. Guo, X. Liu, G. F. Zhao, Y. H. Luo, J. Chem. Phys. 126 (2007) 234704.
- [16] M. J. Frisch, G. W. Trucks, H. B. Schlegel, *et al.*, Gaussian 09, Rev. A.02 (Gaussian, Inc., Wallingford CT, 2009).
- [17] G. von Helden, A. Kirilyuk, D. van Heijnsbergen, *et al.*, Chem. Phys. 262 (2000) 31.
- [18] G. Herzberg, Molecular Spectra and Molecular Structure II, Infrared and Raman Spectra of Polyatomic Molecules (van Nostrand-Reinhold, New York, 1945).