

# A new hypermetallic molecule LaOMn generated by laser ablation

Xue-feng Wang, Hai-jun Dang, Zhen-ning Gu, Qi-zong Qin \*

*Laser Chemistry Institute, Fudan University, Shanghai 200433, China*

Received 7 May 1998; in final form 5 November 1998

## Abstract

A new hypermetallic oxide LaOMn and its positive ion involving two heterometal atoms were observed and identified in the 532 nm laser ablation of a  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$  target using both time-resolved quadrupole mass spectrometric and time-of-flight mass spectrometric techniques. The dependence of  $\text{LaOMn}^+$  yield on the laser fluence also confirmed the formation of the ionic hypermetallic species. Theoretical calculations were carried out to predict the stability and the geometric structures of these new molecules. The calculations suggest that the LaOMn and  $\text{LaOMn}^+$  molecules might be formed via secondary reactions of the neutral and ionic MnO with La or  $\text{La}^+$  in the laser ablated plasma. © 1999 Elsevier Science B.V. All rights reserved.

## 1. Introduction

The investigations of the hypermetallic molecules such as  $\text{A}_n\text{O}$ ,  $\text{A}_n\text{S}$ ,  $\text{A}_n\text{C}$  and  $\text{A}_n\text{CN}$ , with metal atom,  $\text{A} = \text{Li}, \text{Na}, \text{K}, \text{Mg}, \text{or Al}$ , have attracted considerable attention since the early 1980s [1–8]. Many hyperlithiated molecules, including closed-shell  $\text{Li}_6\text{C}$  molecule and open-shell radicals, such as  $\text{Li}_3\text{O}$ ,  $\text{Li}_3\text{S}$  and  $\text{Li}_4\text{P}$ , have been studied experimentally by Kudo and his coworkers [8–12]. Previous studies provided evidence that the main characteristics of these molecules are their unusual stoichiometries and unexpected hypervalent bonding with thermodynamic stability [13,14]. The hypermetallic molecules have been generated by laser ablation [15] and high-temperature reactions in a Knudsen cell

[6,8–12,16], and the time-of-flight (TOF) mass spectrometry and Knudsen-effusion mass spectrometry were employed to identify these molecules. In the theoretical studies, ab initio calculations have proven to be a powerful method to predict the structure, stability and other physical properties of these new molecules [8,17].

Recently, a Glasgow group reported the observation of a hypermetallic molecule  $\text{K}_2\text{CN}$  generated by 266 nm pulsed laser ablation of solid  $\text{K}_3\text{Fe}(\text{CN})_6$ , both the  $\text{K}_2\text{CN}^+$  ions and the neutral  $\text{K}_2\text{CN}$  molecules have been detected by a reflection TOF mass spectrometer [18]. They argued that these hypermetallic molecules have many features of structures similar to those of  $\text{Li}_2\text{CN}$  investigated by Kudo et al. [8]. In addition, they reported the readily generation of a new molecule  $\text{Si}_2\text{N}$  by laser ablation of  $\text{Si}_3\text{N}_4$  target [15]. Although many hypermetallic molecules have been investigated experimentally and

\* Corresponding author. Fax: +86 21 6510 2777; e-mail: qzqin@fudan.ac.cn

theoretically, there is no report so far on a novel molecule which consists of two heterometal atoms and one electronegative atom. Recently we have studied the mass and velocity distributions of the laser ablated species from a colossal magnetoresistant  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$  (La–Ca–Mn–O) target [19]. Novel molecules  $\text{LaOMn}$  and  $\text{Mn}_2\text{O}$  as well as their positive ions were observed by time-resolved quadrupole mass spectrometry.

In this Letter we report the experimental observation of the existence of the  $\text{LaOMn}$  and  $\text{LaOMn}^+$  molecules involving two hetero-metal atoms. Both time-resolved quadrupole mass spectrometric (QMS) and TOF mass spectrometric (TOF-MS) techniques were employed to identify these new hypermetallic molecules. The structure and stability of  $\text{LaOMn}$  molecule and  $\text{LaOMn}^+$  ion were predicted theoretically, and their possible formation pathways were also discussed.

## 2. Experimental

The apparatus used for laser ablation and QMS detection has been described previously [20]. Briefly, a stainless steel ablation chamber was evacuated down to a pressure of  $10^{-4}$  Pa, and a rotatable target holder was situated at the center of the chamber. A quadrupole mass spectrometer (QMS, ULVAC MSQ-400) was housed in a detection chamber which was sitting in the ablation chamber and was evacuated to  $10^{-8}$  Pa by two ion pumps. The distance between the ionizer of QMS and the target sample surface is 18 cm. The laser beam at 532 nm was provided by the second harmonic frequencies of a Q-switched Nd:YAG laser (Spectra-Physics GCR-190) and focused onto the sample surface with an angle of  $45^\circ$  to the surface normal. The laser was operated with a pulse width of 6 ns and a repetition rate of 10 Hz. The laser intensity was measured by a powermeter with a pyroelectric detector. The mass distributions of the neutral and ionic ablated species were determined with the QMS. For detecting the genuine ionic species, the ionizer of QMS was switched off, and both ablated ionic and neutral species were detected with the ionizer switched on. The TOF spectra of ablated species were recorded

with a 10 MHz transient recorder interfaced to a PC computer. The signal intensities or relative yields of the ablated species were obtained by integrating the corresponding TOF spectra.

A laser ablation/ionization linear TOF-MS, which consists of an ablation chamber and a flight tube of 1.3 m length, was employed to detect the ablated positive ions. The TOF-MS system was pumped by two turbomolecular pumps to a base pressure of  $10^{-5}$  Pa. The 532 nm laser beam was incident along the surface normal and focused onto the sample surface. The ablated ions passed through an orifice leading to the extraction field, where they were extracted perpendicularly by a pulsed high voltage (1800 V). After drifting over the flight tube, the ions were detected by a dual microchannel plate detector with a gain of  $10^7$ , and the ion signals were transferred to a 100 MHz transient recorder for measuring the TOF mass spectra. The time delay between the ablation laser pulse and high-voltage extraction pulse was controlled by a pulse delay generator. Data acquisition and storage were performed with a PC computer.

The La–Ca–Mn–O target pellet was prepared by uniaxially compressing a mixture of  $\text{MnO}_2$ ,  $\text{La}_2\text{O}_3$ , and CaO (AR) with a nominal composition of  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$  and calcinated at  $800^\circ\text{C}$  for 5 h.

## 3. Results and discussion

The typical mass spectra of ionic and neutral ablated species generated from 532 nm laser ablation of a La–Ca–Mn–O target at a fluence of  $1.5 \text{ J/cm}^2$  are shown in Fig. 1. It can be seen that both ionic and neutral  $\text{LaOMn}$  at  $m/e = 210$  are observed. It is interesting that another hypermetallic molecule  $\text{Mn}_2\text{O}$  at  $m/e = 126$  is also observed. Since the natural isotopic abundance of  $^{55}\text{Mn}$ ,  $^{139}\text{La}$  and  $^{16}\text{O}$  for these elements are 100%, 99.91% and 99.76%, respectively, it is reasonable to suggest that the mass peaks at  $m/e = 210$  and  $m/e = 126$  should be assigned to the hypermetallic molecules  $\text{LaOMn}$  and  $\text{Mn}_2\text{O}$ , respectively. It should be noted that another possible ablated species with  $m/e = 210$  is  $\text{CaLaO}_2$ , but it seems very difficult for a tetra-atomic molecule to be formed under our experimental conditions. To

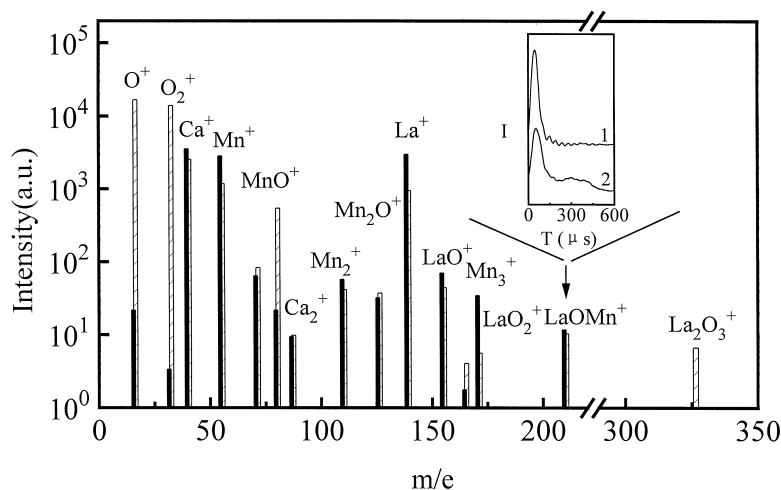


Fig. 1. The mass distributions of ionic (solid) and neutral (shadow) laser ablated species from a La–Ca–Mn–O target at 532 nm. Insert: TOF spectra of  $m/e = 210$  species measured with ionizer off (1) and on (2), respectively.

exclude the possibility of the  $\text{CaLaO}_2$  formation, a similar ablation experiment was carried out using a  $\text{CaO}/\text{La}_2\text{O}_3$  (1:1 mole ratio) target and no signal was detected at  $m/e = 210$ . As shown in Fig. 1, the relative signal intensities of positive ions  $\text{LaOMn}^+$  and  $\text{Mn}_2\text{O}^+$  are higher than those of neutral molecules  $\text{LaOMn}$  and  $\text{Mn}_2\text{O}$ . But it is difficult to expect that the neutral  $\text{LaOMn}$  and  $\text{Mn}_2\text{O}$  molecules are less stable than the ionic species because the neutral ablated species are detected with the ionizer of QMS switched on, and the  $\text{LaOMn}$  and  $\text{Mn}_2\text{O}$  molecules might be cracked by 70 eV electron impact although there are no information on the cracking cross section of these new molecules.

The TOF spectra for both ionic and neutral  $\text{LaOMn}$  molecules were measured by a time-resolved QMS with the ionizer switched off and on, respectively. As shown in the insert of Fig. 1, the TOF spectrum of ionic  $\text{LaOMn}^+$  (curve 1) shows only one component peaked at 45  $\mu\text{s}$ , while there appear two components for neutral  $\text{LaOMn}$  (curve 2), corresponding to a fast one and a slow one. It can be seen that the peak position of the fast component is close to that of the genuine ions and due to the contribution of  $\text{LaOMn}^+$  ions, and the slow and broad component peaked at  $\sim 300 \mu\text{s}$  might be contributed by the neutral  $\text{LaOMn}$  species. From the TOF spectra, the most probable velocities of the ionic  $\text{LaOMn}^+$  and neutral  $\text{LaOMn}$  are estimated to be  $4.0 \times 10^3 \text{ m/s}$  and  $0.6 \times 10^3 \text{ m/s}$ , respectively,

which are close to those for other ablated species such as  $\text{MnO}^+$  and  $\text{MnO}$  [19].

The laser ablation/ionization TOF-MS technique was also employed to identify the hypermetallic oxide  $\text{LaOMn}^+$  generated from the ablation of a La–Ca–Mn–O target. Fig. 2 shows a TOF mass spectrum of ablated ions at 532 nm with a fluence of  $0.6 \text{ J/cm}^2$ . It can be seen that besides the metallic ions  $\text{Ca}^+$ ,  $\text{Mn}^+$  and  $\text{La}^+$ , ionic species  $\text{LaO}^+$  and

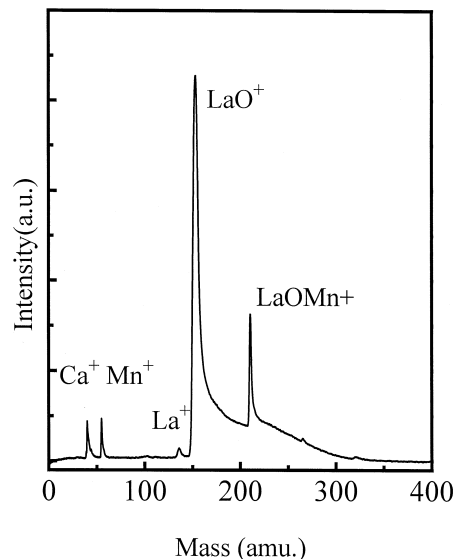


Fig. 2. A TOF mass spectrum of ionic ablated species from laser ablation of a La–Ca–Mn–O target at 532 nm.

LaOMn<sup>+</sup> are observed with comparable signal intensities. The long tails of the peaks for heavy ablated species such as LaO<sup>+</sup> and LaOMn<sup>+</sup> ions suggest that these ionic species have a broader velocity distribution and are probably formed via the secondary reactions between the ablated species in the laser plasma plume.

To further confirm the formation of LaOMn<sup>+</sup>, the laser fluence effect on the signal intensity of LaOMn<sup>+</sup> was examined. Fig. 3a gives  $m/e = 210$  signals measured at different laser fluence. It can be seen that the signal intensity of LaOMn<sup>+</sup> is enhanced by increasing the laser fluence. The ablation yield of LaOMn<sup>+</sup> is obtained by integrating the peak of  $m/e = 210$  in the TOF mass spectrum, and Fig. 3b presents the ablation yield of LaOMn<sup>+</sup> as a

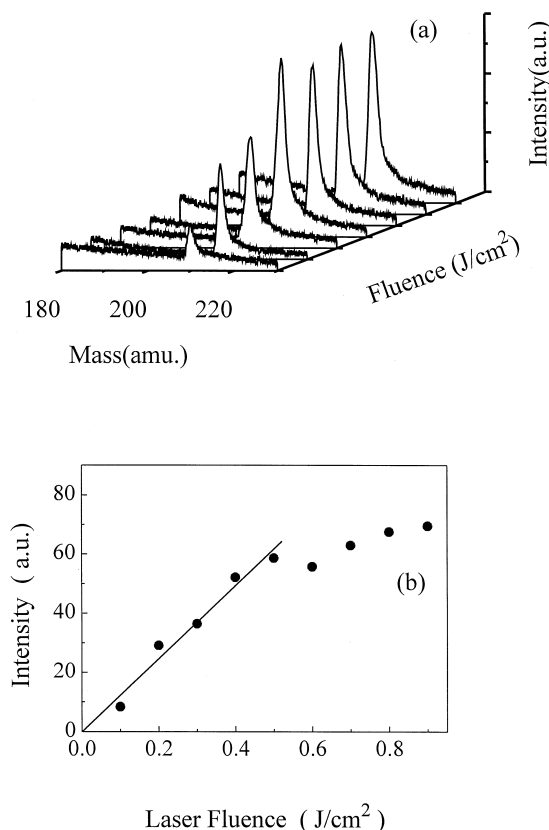


Fig. 3. The measured signal of ionic LaOMn<sup>+</sup> species ( $m/e = 210$ ) at different laser fluence (a), and the plot of the integrated intensity versus laser fluence (b).

function of the laser fluence. It is found that the measured LaOMn<sup>+</sup> signal increases linearly with the increase of the laser fluence up to 0.50  $J/cm^2$  and seems to be saturated in higher fluence region. This result is evident to clarify the existence of the ionic LaOMn<sup>+</sup>, and implies that there exists a competing reaction pathway against the formation of LaOMn<sup>+</sup> at higher laser fluence.

In order to predict the stability and the structures of the LaOMn<sup>+</sup> and LaOMn molecules, the theoretical calculations were performed to provide the geometric parameters and structure features of the new hypermetallic molecules. Geometry of both the ionic LaOMn<sup>+</sup> and the neutral LaOMn molecules were optimized at MP2(FU)/LANL2DZ to find the global minima using GAUSSIAN94 package of computer codes [21,22]. Electron correlation was considered via Møller–Plesset perturbation theory to the second order (MP2). The D95 basis set built in the program was employed for oxygen atoms and LANL2DZ basis set with an Ar-like effective core potential (ECP) [21–24] was used for La and Mn atoms. Generally, the Mn and La atom basis sets are described with an explicit 7 and 3 electrons valence shell, respectively, with the chemically less active core electrons pictured with effective potentials. Due to the degeneracy of the ground state and low-lying excited states for the investigated systems, the virtual orbitals were allowed to mix into the occupied space in the self-consistent field (SCF) using fractional occupations of orbitals close to the Fermi level. Fundamental frequencies were obtained with the calculated complete quadratic force constant matrices at the optimized structures. The MP2 equilibrium geometries were used to evaluate electron correlation by Møller–Plesset perturbation theory to full fourth order (MP4SDTQ) with the same basis sets.

Geometric parameters and vibrational frequencies of the LaOMn<sup>+</sup> and LaOMn molecules are listed in Table 1. Since the quartet of OMnO and sextet of MnO were found to be the most stable states in ESR and IR measurements [25–27], it is reasonable to infer that the most stable states of LaOMn and LaOMn<sup>+</sup> are higher multiplicity. Our calculation result shows that the quintuplet state for LaOMn is found while the sextet state is converged for LaOMn<sup>+</sup>. As shown in Table 1, the bond length of the Mn–O bond is little shorter than that of the

Table 1

Geometries, total energies ( $E$ ) and unscaled vibrational frequencies for LaOMn, LaOMn<sup>+</sup> and other correlated ablated species at the MP2 level

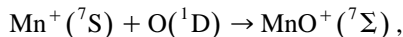
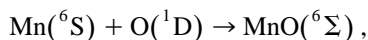
Species	Multiplicity	$E$ (MP4) <sup>a</sup> (hartree)	Geometry	Frequency (cm <sup>-1</sup> )
LaOMn	5	-209.166652	$R_{\text{LaO}} = 2.19 \text{ \AA}$ $R_{\text{MnO}} = 1.84 \text{ \AA}$ $A = 174.6^\circ$	875.6(489.0) <sup>b</sup> 271.9(8.5) 184.9(4.2)
LaOMn <sup>+</sup>	6	-209.043777	$R_{\text{LaO}} = 2.12 \text{ \AA}$ $R_{\text{MnO}} = 1.88 \text{ \AA}$ $A = 180.0^\circ$	805.1(659.8) 246.9(2.9) 114.6(29.4)
LaO	2	-105.930360	$R = 2.031 \text{ \AA}$	822.4(339.9)
LaO <sup>+</sup>	1	-105.796919	$R = 2.018 \text{ \AA}$	728.0(12.1)
MnO	6	-178.131544	$R = 1.939 \text{ \AA}$	627.2(53.6)
MnO <sup>+</sup>	7	-177.942003	$R = 1.844 \text{ \AA}$	708.0(103.8)
O	1	-74.754957		
La	2	-30.8507510		
La <sup>+</sup>	1	-30.630842		
Mn	6	-103.220977		
Mn <sup>+</sup>	7	-103.073228		

<sup>a</sup>Calculated using the MP2 optimized geometries and frequencies.

<sup>b</sup>IR intensity in parentheses (km mol<sup>-1</sup>).

La–O bond in these molecules. The bond angle of the ionic triatomic molecule LaOMn<sup>+</sup> is 180°; however, the bond angle of the neutral LaOMn is 174.6°, which might be expected as a result of Jahn–Teller distortion. In addition, the calculated frequency of LaO was found to be 822.4 cm<sup>-1</sup>, in agreement to the available experimental value of 811.6 cm<sup>-1</sup>. Accordingly, our theoretical calculations give more evidence for the existence of the ionic and neutral hetero-hypermetallic oxides LaOMn<sup>+</sup> and LaOMn.

The formation of the LaOMn can be simply described by the secondary reactions underlying a laser ablation of a La–Ca–Mn–O target. It is well known that the ablated metal atoms and ions can easily react with the O atoms to form binary metal oxides in the laser plasma plume near the target. In order to evaluate the accuracy of the calculated energy change  $\Delta E$  values for the hypermetallic oxide formation, the energy changes for the following processes:



were calculated and found to be -3.78 and -3.1 eV, respectively, which are close to the experimental values  $-3.7 \pm 0.17$  eV [28] and  $-2.53 \pm 0.6$  eV [29]. In addition, the calculated  $\Delta E$  for the formation of LaO is -8.8 eV, also in agreement with the

experimental value of -8.3 eV [30]. Then we calculated the energy changes  $\Delta E$  for different possible pathways to form hypermetallic molecule LaOMn and its positive ion based on the calculated total energies of LaOMn and other species listed in Table 1. The calculated results are summarized in Table 2. Energetically, the highly exothermic reactions (1), (2) and (3) are more favorable to form the LaOMn and LaOMn<sup>+</sup> molecules. These secondary reactions probably have low activation barriers, and the collisional probabilities of the ablated La and MnO species play an important role for the formation of these new molecules. Because of the lack of extensive information on the reaction products and intermediates, a detailed examination of the potential

Table 2

Possible reaction pathways and reaction energy changes

Reaction	$\Delta E$ (eV)	
$\text{La}^+(^1\text{S}) + \text{MnO}(^6\Sigma) \rightarrow \text{LaOMn}^+(^6\Sigma)$	-7.658	(1)
$\text{La}(^2\text{D}) + \text{MnO}^+(^7\Sigma) \rightarrow \text{LaOMn}^+(^6\Sigma)$	-9.506	(2)
$\text{La}(^2\text{D}) + \text{MnO}(^6\Sigma) \rightarrow \text{LaOMn}(^5\Sigma)$	-5.017	(3)
$\text{Mn}(^6\text{S}) + \text{LaO}(^2\Sigma) \rightarrow \text{LaOMn}(^5\Sigma)$	-0.416	(4)
$\text{Mn}(^6\text{S}) + \text{LaO}^+(^1\Sigma) \rightarrow \text{LaOMn}^+(^6\Sigma)$	-0.703	(5)
$\text{Mn}^+(^7\text{S}) + \text{LaO}(^2\Sigma) \rightarrow \text{LaOMn}^+(^6\Sigma)$	-1.093	(6)

enrage surfaces is difficult. Apparently, the reaction mechanisms for the formation of LaOMn and its ion are complicated and the details of the reaction pathways should be further investigated.

#### 4. Conclusions

Both time-resolved QMS and TOF-MS techniques are successfully used to identify the new hetero-hypermolecular molecule LaOMn and its positive ion generated by pulsed laser ablation of a La–Ca–Mn–O target. The theoretical calculations suggest that the LaOMn( $^5\Sigma$ ) and LaOMn $^+$ ( $^6\Sigma$ ) are stable, and their geometric structures nearly belong to a linear molecules. Based on the energetic consideration, both the LaOMn and LaOMn $^+$  molecules might be produced mainly via the secondary reactions in the laser ablated plasma such as La( $^2D$ ) + MnO( $^6\Sigma$ )  $\rightarrow$  LaOMn( $^5\Sigma$ ) and La( $^2D$ ) + MnO $^+$ ( $^7\Sigma$ )  $\rightarrow$  LaOMn $^+$ ( $^6\Sigma$ ).

#### References

- [1] P.v.R. Schleyer, E.U. Wurthwein, J.A. Pople, *J. Am. Chem. Soc.* 104 (1982) 5839.
- [2] P.v.R. Schleyer, E.U. Wurthwein, E. Kaufmann, T.J. Clark, *J. Am. Chem. Soc.* 105 (1983) 5930.
- [3] P.v.R. Schleyer, B. Tidor, E.D. Jemmis, J. Chandrasekhar, E.U. Wurthwein, A.J. Kos, B.T. Luke, J.A. Pople, *J. Am. Chem. Soc.* 105 (1983) 484.
- [4] P.v.R. Schleyer, A.E. Reed, *J. Am. Chem. Soc.* 110 (1988) 4453.
- [5] A.E. Reed, P.v.R. Schleyer, R.J. Janoschek, *J. Am. Chem. Soc.* 113 (1991) 1885.
- [6] Y. Xie, F. Schaefer III, *Chem. Phys. Lett.* 179 (1991) 563.
- [7] P.D. Dao, K.L. Peterson, A.W. Castleman Jr., *J. Chem. Phys.* 80 (1984) 563.
- [8] H. Kudo, M. Hashimoto, K. Yokoyama, C.H. Wu, A.E. Derigo, F.M. Bickelhaupt, P.v.R. Schleyer, *J. Phys. Chem.* 99 (1995) 6477.
- [9] H. Kudo, *Nature* 355 (1992) 432.
- [10] H. Kudo, K. Yokoyama, C.H. Wu, *J. Chem. Phys.* 101 (1994) 4190.
- [11] H. Kudo, K.F. Zmbov, *Chem. Phys. Lett.* 87 (1991) 77.
- [12] C.H. Wu, H. Kudo, H.R. Ihle, *J. Chem. Phys.* 70 (1979) 1815.
- [13] C.J. Marsden, *J. Chem. Soc., Chem. Commun.* (1989) 1356.
- [14] J. Ivanic, C.J. Masden, *J. Am. Chem. Soc.* 115 (1993) 7503.
- [15] S.L. Wang, K.W.D. Ledingham, W.J. Jia, R.P. Singhal, *Appl. Surf. Sci.* 93 (1990) 205.
- [16] J.W. Chinn Jr., R.J. Lagow, *J. Am. Chem. Soc.* 106 (1984) 3694.
- [17] A.I. Boldyrev, I.L. Shamovsky, P.v.R. Schleyer, *J. Am. Chem. Soc.* 114 (1992) 6469.
- [18] S.L. Wang, K.W.D. Ledingham, R.P. Singhal, *J. Phys. Chem.* 100 (1996) 11282.
- [19] H.J. Dang, Z.H. Han, Q.Z. Qin, *Science in China A* 41 (1998) 1309.
- [20] Q.Z. Qin, Z.H. Han, H.J. Dang, *J. Appl. Phys. A* 83 (1998) 6082.
- [21] P.J. Hay, W.R. Wadt, *J. Chem. Phys.* 82 (1985) 270.
- [22] M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G. Johnson, M.A. Robb, J.R. Cheeseman, T.A. Keith, G.A. Petersson, J.A. Montgomery, K. Raghavachari, M.A. Al-Laham, V.G. Zakrzewski, J.V. Ortiz, J.B. Foresman, J. Cioslowski, B.B. Stefanov, A. Nanayakkara, M. Challacombe, C.Y. Peng, P.Y. Ayala, W. Chen, M.W. Wong, J.L. Andres, E.S. Replogle, R. Gomoerts, R.L. Martin, D.J. Fox, J.S. Binkley, D.J. Defrees, J. Baker, J.P. Stewart, M. Head-Gordon, C. Gonzalez, J.A. Pople, GAUSSIAN94, Revision B2, Gaussian, Pittsburgh, PA, 1995.
- [23] W.R. Wadt, P.J. Hay, *J. Chem. Phys.* 82 (1985) 184.
- [24] P.J. Hay, W.R. Wadt, *J. Chem. Phys.* 82 (1985) 299.
- [25] R.F. Ferrante, J.L. Wilkerson, W.R.M. Graham, W. Weltner Jr., *J. Chem. Phys.* 67 (1977) 5904.
- [26] G.V. Chertihin, L. Andrews, *J. Phys. Chem.* 101 (1997) 8547.
- [27] K.P. Huber, G. Herzberg, *Molecular Spectra and Molecular Structure, Vol. IV*, Van Nostrand Reinhold Canada, 1979.
- [28] C.J. Cheetam, R.F. Barrow, *Adv. High. Temp. Chem.* 1 (1967) 7.
- [29] P.B. Armentrout, L.F. Halle, J.L. Beauchamp, *J. Chem. Phys.* 76 (1982) 2449.
- [30] R.C. Weast (Ed.), *Handbook of Chemistry and Physics*, 58th edn., CRC Press, Ohio, 1978.