Physics Letters A ••• (••••) •••–•••

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Physics Letters A

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$Ti_{12}Xe$: A twelve-coordinated Xe-containing molecule

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ARTICLE INFO

Article history:
Received 14 January 2017
Received in revised form 31 March 2017
Accepted 25 May 2017
Available online xxxx
Communicated by R. Wu

Keywords:
Xenon
Coordination number
Density functional theory
Xenon–titanium cluster complex
Chemical bonding

ABSTRACT

A twelve-coordinated Xe-containing molecule $Ti_{12}Xe$ has been predicted by DFT calculations with quasi-icosahedral symmetry. Structural and NBO analyses show the chemical bonding exists between the central Xe atom and peripheral Ti atoms, which leads to the high stability of the molecule to a considerable degree. First principle molecular dynamics simulations further reveal the particularly high thermal stability of $Ti_{12}Xe$ up to 1500 K. This unique species may disclose new physics and chemistry of xenon element and stir interest in the Xe-transition metal cluster physics and chemistry.

1. Introduction

Noble gases are a unique class of monoatomic molecules at room temperature, with fully filled *s* and *p* valence orbitals and thus extremely low reactivity. They are thus appears quite inert in the vast majority of chemical reactions. Since the preparation of the first noble gas compound $Xe^+[PtF_6]^-$ by Bartlett [1], searching for the new compounds of noble gas becomes a very intriguing topic. $(Au^{II}Xe_4)(Sb_2F_{11})$, as the first experimentally separated compound containing a Xe-metal bond, created significant interest in the chemistry of noble gases and noble metals [2]. LeBlond et al. synthesized the first Xe–N bond containing compound $FXeN(SO_2F)_2$, which paved the way for further developments of Xe–N chemistry [3]. Bartlett and co-workers prepared the first homoleptic coordination compound of XeF_2, $Ag(XeF_2)_2(AsF_6)$, attracting great attention to the coordination chemistry of XeF_2 [4]. Zhu et al. computationally predicted that Xe and Fe/Ni can form intermetallic compounds under Earth inner core's temperature and pressure, which may explain the mystery of "missing xenon" [5]. Dewaele et al. synthesized and studied the stability of xenon oxides Xe_2O_5 and Xe_3O_2 under high pressure where they found that both form extended networks and adopt mixed oxidation states [6]. After half century's efforts, more than half a thousand of noble gas compounds have been synthesized and identified though [7–13], the knowledge of the structures and properties of these compounds is still very limited which motivates us to explore the scope of the noble gas chemistry and to deepen the understanding of the nature of the noble gas elements.

Coordination number (CN) is a fundamental factor governing the molecular structure. New coordination numbers often create novel chemical bonding mode and extend the boundary of our understanding of the molecules. To date, a large number of high coordination number species have been found [14–21]. Wang and co-workers have observed the highly symmetric cobalt-centered boron drum-like structures of CoB_{16}^-, with the highest CN of 16 found so far [14]. Pollak et al. have prepared another highest CN molecule $Cs[H_2NB_2(C_6F_5)_6]$, in which a central cesium atom is coordinated by 16 fluorine atoms [15]. Galeev et al. observed the highest CN planar species $Ta©B_{10}^-$ and $Nb©B_{10}^-$ anions, with a CN of 10 [16]. By using Pb^{2+} and He, Hermann et al. predicted a 15 coordinated species of $PbHe_{15}^{2+}$ [17]. We are inspired by these studies to search the high CN species containing Xe to gain more insight into the chemical bonding nature of Xe. To the best of our knowledge, XeF_8 and XeF_8^{2-} are the Xe's highest CN molecular species reported to date [22,23]. A natural question to ask is 'can Xe form stable molecules with higher CN?'. Our recent study reveals a pseudospherical quasi-icosahedral molecule $Ti_{12}Xe$ with a higher CN of 12 towards Xe. Analogous to previous reported magic metal clusters [18–21], such as $Au_{12}W$, $Al_{12}Si$, and Ti_{13}, $Ti_{12}Xe$ is highly stable as well. Our calculations show that there is substantial chemical bonding between Xe and Ti atoms, and the species can keep sphere-like at temperature up to 1500 K.

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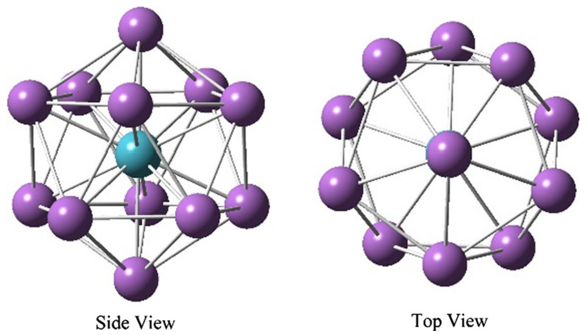
http://dx.doi.org/10.1016/j.physleta.2017.05.052

Please cite this article in press as: J. Miao et al., $Ti_{12}Xe$: A twelve-coordinated Xe-containing molecule, Phys. Lett. A (2017), http://dx.doi.org/10.1016/j.physleta.2017.05.052



Side View Top View

Fig. 1. Optimized quasi-icosahedral structure of $Ti_{12}Xe$. Medium turquoise sphere denotes the xenon atom in the center, and purple spheres represent titanium atoms.

2. Computational details

Initially, we optimized the $Ti_{12}Xe$ at the B3LYP level of theory [24,25], with basis sets of SDD [26] for Ti atoms and aug-cc-pVTZ-PP [27] for Xe atom. Then harmonic vibrational frequency analyses were carried out to identify whether it is a real local minimum on the potential energy surface. The natural bond orbital (NBO) analyses were conducted to obtain the partial atomic charges and Wiberg bond indexes [28] of the optimized $Ti_{12}Xe$. Furthermore, we did the above mentioned calculations by using density functionals of M06 [29], B3PW91 [30], PBE0 [31] and B3P86 [32] to make a mutual corroboration with the B3LYP calculations on $Ti_{12}Xe$. All of the calculations were performed using Gaussian 09 package [33]. All of the default settings in the package were used except integration grid, for which the grid at ultrafine level was used in all calculations to provide more reliable results.

To test the thermal stability of $Ti_{12}Xe$, first principle molecular dynamics simulations were performed in the canonical ensemble, with using the Nose–Hoover thermostat and a time step of 1 fs, and at a finite temperature of 1500 K. The exchange correlation potential was described by the generalized-gradient approximation (GGA) with the spin-polarized functional of Perdew–Burke–Ernzerh (PBE) [34]. Wavefunctions were expanded in triple-ζ Gaussian basis sets with an auxiliary plane-wave basis and a cutoff energy of 300 Ry. Core electrons were modeled by scalar relativistic norm-conserving pseudopotentials [35,36] with 4, 8 valence electrons of Ti, Xe, respectively. Brillouin zone integration was performed with a reciprocal space mesh consisting of only the Γ-point. CP2K package was used for these simulations [37,38].

3. Results and discussion

The optimized geometry of $Ti_{12}Xe$ at B3LYP level of theory is shown in Fig. 1 (the results of other selected density functionals are quite analogous to these of B3LYP, unless specified otherwise, the results of B3LYP are adopted below). It is a quasi-icosahedral molecule, with the Xe atom at the center and chemically bound to the peripheral twelve Ti atoms. The predicted harmonic frequencies of $Ti_{12}Xe$ are given in Table 1. The results indicate that the species is a true local minimum on the potential surface. The lowest vibrational frequency is 90.3 cm^{-1} at the B3LYP level and 75.0 cm^{-1} at the M06 level, which are sufficiently large to meet a stability criterion suggested by Hoffmann et al. [39]. Other functionals reach the same conclusion as B3LYP. Analogous to XeAuF molecule [40], cluster $Ti_{12}Xe$ has no strong stretching modes involving Xe atom. As to the energy gap between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), the calculated results give ~0.80 eV at the B3LYP level and ~0.97 eV at the M06 level. Both are consistently quite large, which further supports the viability of the molecule [39].

Table 1
Several key parameters of $Ti_{12}Xe$ optimized by B3LYP and several other functionals with the basis sets of SDD for Ti and aug-cc-pVTZ-PP for Xe.

Method	B3LYP	M06	PBE0	B3PW91	B3P86
Average Bond Length (Å)					
Xe–Ti	2.610	2.597	2.581	2.588	2.587
Ti–Ti	2.746	2.731	2.714	2.697	2.712
HOMO	−3.64	−3.85	−3.79	−3.69	−4.22
LUMO	−2.84	−2.88	−2.80	−2.89	−3.42
Harmonic Vib. (cm^{-1})					
Lowest	90.3	75.0	101.8	101.2	98.5
Highest	343.8	359.0	363.7	357.4	361.8

Table 2
Several relevant parameters of the optimized quasi-icosahedral Ti_{13} at B3LYP level, with SDD basis set on Ti atoms. Ti–Ti_{center}, the average distance in Å between the central Ti atom and the other Ti atoms on the Ti shell; Ti–Ti, the average distance in Å between adjacent Ti atoms on the Ti shell; $q_{Ti(center)}$, $q_{Ti(shell)}$, the partial atomic charges in electron (NBO) on the central Ti atom and on the Ti shell, respectively.

Ti–Ti_{center}	Ti–Ti	$q_{Ti(center)}$	$q_{Ti(shell)}$
2.631	2.758	−2.0	2.0

For most of noble gas compounds reported so far, they are generally metastable under ambient conditions. However, they can be synthesized by some special techniques at a sufficiently low temperature where the protecting barriers are able to prevent them from dissociation, such as HXeOXeH [41], $(C_6H_5)_2Xe$ [42], $(Au^{II}Xe_4)(Sb_2F_{11})$ [2]. For example, HXeOXeH is higher than Xe + HXeOH by 4.57 eV in electronic energy and the corresponding decomposition barrier is just 0.57 eV. Nevertheless, it can be prepared by photolysis of water in solid xenon and subsequent annealing at 40-45K [41]. $Ti_{12}Xe$ is metastable as well with respect to Ti_{12} (cage) + Xe. The release of xenon atom from the titanium cage is thus exoergic. $Ti_{12}Xe$ possesses at least an additional of 6.6 eV as compared to Xe + Ti_{12} (Ti_{12} is the global energy minimum from Ref. [21]), it may thus be used as a high energy material in some special fields. First principle MD results indicate that the structure of the molecule remains almost intact at an elevated temperature up to 1500 K during the simulation of 10 ps, suggesting a sufficiently high protective barrier exists to prevent the escape of xenon atom from the titanium shell (Fig. 2). This kinetically highly stable species can thus be prepared via an appropriate synthetic procedure.

For the optimized quasi-icosahedral structure of $Ti_{12}Xe$, the Xe–Ti bond lengths range from 2.600 to 2.622 Å, with the average value of 2.610 Å. This average bond distance is a bit shorter than average Ti–Ti_{center} bond distance in the quasi icosahedral Ti_{13} cluster (2.631 Å) (Table 2). It is worth noting that the average Xe–Ti bond length is within the sum of covalent bonds of Xe and Ti atoms of 2.660 Å [43], and substantially lower than the corresponding van der Waals radius sum of 4.210 Å [44]. This means the chemical bonding exists between Xe and peripheral Ti atoms.

The calculated Wiberg bond indices (WBI) [28] of Xe–Ti bonds of $Ti_{12}Xe$ are at 0.284~0.299, further suggesting the formation of Xe–Ti chemical bond, in accord with the above discussion on bond lengths. The calculated average WBI for adjacent Ti atoms equals 0.902 in $Ti_{12}Xe$. The partial atomic charges (NBO) of $Ti_{12}Xe$ show that valence electrons of Xe are activated and a substantial negative charges (1.8 e) are transferred from Xe to Ti atoms in the compound. The number of valence electrons on the skeletal Ti cage is very close to 50 ($12 \times 4 + 1.8$), approximately meeting Wade's $4n + 2$ rule [45]. This indicates that the central atom tends to donate some electrons to the Ti shell (or vice versa) to make the close coordination compound obey the $4n + 2$ rule, and then to stabilize it. This holds for other analogues such as Ti_{13} for which the shell donates two electrons to the central atom (Table 2). The

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