Computational and Theoretical Chemistry 991 (2012) 48–55

Contents lists available at SciVerse ScienceDirect

Computational and Theoretical Chemistry

journal homepage: www.elsevier.com/locate/comptc

Rare gas bond property of $Rg–Be_2O_2$ and $Rg–Be_2O_2–Rg$ (Rg = He, Ne, Ar, Kr and Xe) as a comparison with Rg–BeO

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ARTICLE INFO

Article history:
Received 28 December 2011
Received in revised form 21 March 2012
Accepted 22 March 2012
Available online 1 April 2012

Keywords:
Rare gas bond
Ab initio calculation
Bond property

ABSTRACT

We have investigated the bond properties of $Rg–Be_2O_2$ and $Rg–Be_2O_2–Rg$ and compared to that of Rg–BeO by using high level quantum chemical calculation. It is found that more than half of the binding energies for all $Rg–Be_2O_2$ complexes come from the contribution of the electron correlation. However, in the series of Rg–BeO, the influences of the electron correlation to the binding energies are much smaller than those of $Rg–Be_2O_2$ series. These results indicate that the rare gas bonds are more van der Waals nature in $Rg–Be_2O_2$ cases. The strong van der Waals nature of $Rg–Be_2O_2$ series result in the monotonous increment of the bonding energy from $He–Be_2O_2$ to $Xe–Be_2O_2$ according to the size dependent orbital distortion of the rare gas atoms. On the other hand, a significant amount of back-donation from $2p_\pi$ on O to $2p_\pi$ on Be is observed in He–BeO. The existence of this mechanism would facilitate the charge transfer from He to BeO and stabilize the He–BeO bond.

1. Introduction

Since Bartlett's discovery of $Xe^+PtF_6^-$ [1,2], the chemistry of the rare gases (Rgs) revealed a fascinating field of experimental and theoretical research. Many rare gas compounds of Kr, Xe and Rn have been found [3–5]. Some Ar [6–12] compounds also have been found. Although no stable compounds containing He and Ne have been observed experimentally yet, some compounds of He and Ne have also been theoretically predicted with computed binding energies of a few kcal mol^{-1} [13–17]. Up to now, several types of rare gas compounds have been studied and predicted [18–26].

Be_2O_2 with a D_{2h} rhombus structure is a candidate which can bind two rare gas atoms. It is because electron affinity of Be_2O_2 was calculated to be about 1 eV [27], and its LUMO extends to both side of Be–Be axis. Motivated from these facts, we investigated the binding energy of a series of rare gas compounds with Be_2O_2 [28]. It was shown that the binding energy increases monotonically from He to Xe in this series. Since the polarizabilities of the rare gas atoms increases in the order of He to Xe monotonically, the monotonic increment of the rare gas binding energy will be expected. But the behavior of the binding energy of $Rg–Be_2O_2$ was different from that of other studies such as BeO [29,30], BeNH [31], $BeNCH_3$ [32], CuF [33,24], etc. In these cases, Ne binging energy was often calculated smallest among five rare gas atoms [29–39].

In this article, we analyze the bond character of $Rg–Be_2O_2$ using precise quantum chemical calculation. In addition, we compared these binding property with Rg–BeO, which is known a most simplest case of linear and quasi-linear molecule that can bind with rare gas atoms. The difference of the order in binding energies between $Rg–Be_2O_2$ and Rg–BeO series will be explained using AIM, NPA and electron correlation analysis.

2. Calculation

The geometry optimizations were performed at frozen-core coupled cluster method, CCSD(T) [40,41], with aug-cc-pVnZ (n = D, T, Q) basis set for O and cc-pVnZ basis set for Be [42,43]. From He to Kr, aug-cc-pVnZ basis sets were used. For Xe, aug-cc-pVnZ-PP with ECP28MDF [44] basis set was used (abbreviated later as VnZ). As some of the values for Be_2O_2 series were already shown in the previous paper [28], we used those values in this work as they were. However, some of them were calculated again using the basis set selected in this work to compare all the Be_2O_2 and BeO series at the same level of theory. All CCSD(T) optimization and frequency calculations were carried out using the MOLPRO 2006 [45]. Energy of complete basis set (CBS) limit was estimated using the results of VnZ (n = D, T and Q) basis sets calculations with the equation [46,47],

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2210-271X/$ - see front matter
http://dx.doi.org/10.1016/j.comptc.2012.03.020

$$E(n) = E_{\mathrm{CBS}} + \frac{a}{n^3}, \tag{1}$$

where a is a constant and n is cardinal number of the basis set ($n = 2$, 3 and 4 for VDZ, VTZ and VQZ, respectively). In this article, electronic energies including both SCF and electron correlation energy were used for estimating the CBS extrapolation energies. Basis set superposition error (BSSE) [48] was computed for binding energy calculations after geometry optimization. The equilibrium geometries were visualized by Gabedit [49] program. Frequency calculation was also carried out with VDZ basis set. No imaginary frequency was calculated for all molecules.

In order to obtain bond character from coupled cluster densities, we used CCSD/VTZ method at the CCSD(T)/VTZ optimized structures. Input files of atoms-in-molecules (AIMs) [50] analysis were generated by Gaussian 09 [51] and analyzed using AIM 2000 package [52]. In particular, we calculated the electron density, ρ, and the Laplacian of the electron density, $\nabla^2\rho$, at the bond critical points (BCPs). Laplacian plots were also visualized. Natural population analysis (NPA) based on CCSD/VTZ was carried out with the NBO 5.9 program [54] via Gaussian 09. The electron density difference plots were generated by subtracting the electron densities of the Rg and BeO (Be_2O_2) units from the Rg–BeO (Rg–Be_2O_2) complex. BeO and Be_2O_2 electron densities were calculated with the optimized geometry of BeO in Rg–BeO and Be_2O_2 in Rg–Be_2O_2, respectively. The molecular orbital and electron density difference were visualized by Gauss View [53].

The effect of electron correlation was evaluated by comparing the result of Hartree–Fock (HF) level and that of CCSD(T) level. Geometry optimizations at HF/VQZ level were carried out. BSSE was included. Especially, the binding energies and bond lengths of Rg–Be were compared with the results calculated at CCSD(T)/VQZ level. The HF calculations were performed using Gaussian 09.

3. Results and discussion

The binding energies calculated at CCSD(T)/CBS level are summarized in Table 1. The optimized geometries at CCSD(T)/VTZ level are shown in Fig. 1. As Frenking and co-workers reported [29] in their work, the binding energy of Ne–BeO is the smallest among the five rare gas complexes in the series of Rg–BeO. This behavior can be seen in Table 1. The ratios of binding energy of Rg–Be_2O_2 to Rg–BeO are 0.46 for the case of Rg = Ar, Kr and Xe, and 0.40 for Rg = Ne case. Although these four ratios are almost similar, only the ratio of He–Be_2O_2 to He–BeO, which is 0.22, is different and smaller than the others. This indicates that He–BeO has different stabilizing mechanism of the rare gas binding to the others. This behavior has been explained frequently [29,33,38] that the Pauli repulsion between occupied p-orbital of Rg and π on the BeO unit would be important in the mechanism of the rare gas binding, which is absent in the case of He–BeO. To discuss the stabilizing mechanism of the rare gas binding more detail, we investigate the bond properties of rare gas with BeO and Be_2O_2.

Table 1
The binding energy of Rg-molecules by CCSD(T)/CBS limit (kcal mol^{-1}). The last column is the ratio of the binding energy of Rg–Be_2O_2 to Rg–BeO.

Rg	Rg–Be_2O_2 (1)	Rg–Be_2O_2–Rg	Rg–BeO (3)	(1)/(3)
He	1.198[a]	2.101[a]	5.505	0.22
Ne	2.100[a]	3.898[a]	5.213	0.40
Ar	5.526[a]	9.943[a]	12.122	0.46
Kr	6.479	11.594	14.065	0.46
Xe	7.642[a]	13.626[a]	16.496	0.46

[a] Ref. [28].

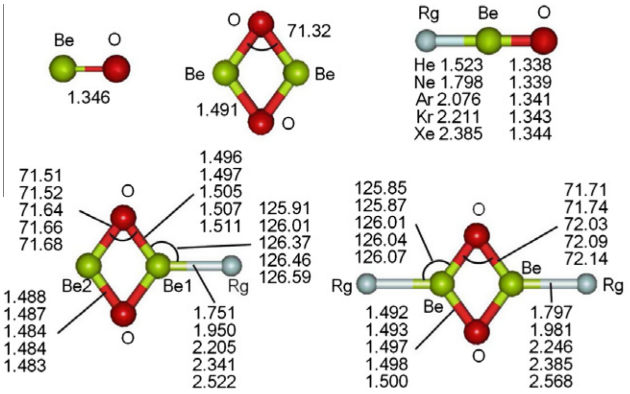

Fig. 1. Equilibrium geometries (length in Å and angles in degrees) at CCSD(T)/VTZ.

3.1. Rg–Be_2O_2

Table 2 shows the results of AIM analysis for all molecules at the CCSD/VTZ level of calculation, which include the bond length between Rg and Be, the distance between BCP and Be, electron density ρ at BCP, and Laplacian concentration of electron density $\nabla^2\rho$ at BCP. The nature of bonding can be quantitatively discussed with the values of ρ and $\nabla^2\rho$ at the BCPs. The value of $\nabla^2\rho < 0$ is related to the shared-type interaction, which indicates that the bonding nature is covalent bond. On the other hand, $\nabla^2\rho > 0$ is related to non-shared-type, closed-shell interactions leading to ionic, hydrogen, and van der Waals bonds [21,32]. Table 2 shows that all Laplacians $\nabla^2\rho$ at BCP of Rg–Be_2O_2 are positive. It indicates that they are all typical closed-shell interactions.

From He to Ar for Rg–Be_2O_2, the electron density ρ at BCP monotonically increases from 0.093 to 0.150 e Å^{-3}. However, from Ar–Be_2O_2 to Xe–Be_2O_2, the electron density at BCP is almost the same value around 0.15 e Å^{-3}. Instead, the Laplacian of electron density at BCP decreases from 3.252 to 2.297 e Å^{-5} through Ar–Be_2O_2 to Xe–Be_2O_2. It indicates that the electron delocalization to BCP becomes large from Ar to Xe. The above results show that, although the basic bond nature of Rg–Be_2O_2 is closed-shell interaction, the delocalization is progressing from Ar to Xe which results in the increment of the binding energy in the order of Ar to Xe.

Laplacian plots of Rg–BeO and Rg–Be_2O_2 are shown in Fig. 2a and b, respectively. Green lines are in regions of electron depletion

Table 2
The results of AIM analysis of the Rg–Be_2O_2, secondary bound Rg–Be_2O_2–Rg and Rg–BeO at the CCSD/VTZ level of theory: The bond length between Be and Rg, $R_{\mathrm{Rg-Be}}$, the distance of the bond critical point (BCP) from the Be atom (both Å), $r_{\mathrm{Be-BCP}}$, electric density, ρ, at BCP (e Å^{-3}), and Laplacian concentration, $\nabla^2\rho$, at BCP (e Å^{-5}).

	Rg	$R_{\mathrm{Rg-Be}}$	$r_{\mathrm{Be-BCP}}$	ρ	$\nabla^2\rho$
Rg–Be_2O_2	He	1.751	0.701	0.093	3.146
	Ne	1.950	0.698	0.101	3.258
	Ar	2.205	0.683	0.150	3.252
	Kr	2.341	0.684	0.155	2.987
	Xe	2.522	0.696	0.158	2.297
Rg–Be_2O_2–Rg	He	1.797	0.717	0.082	2.643
	Ne	1.981	0.709	0.094	2.876
	Ar	2.246	0.690	0.135	3.090
	Kr	2.385	0.697	0.138	2.613
	Xe	2.568	0.709	0.140	2.027
Rg–BeO	He	1.523	0.631	0.198	7.390
	Ne	1.798	0.651	0.158	6.174
	Ar	2.076	0.646	0.219	5.297
	Kr	2.211	0.656	0.221	4.291
	Xe	2.385	0.668	0.228	3.218