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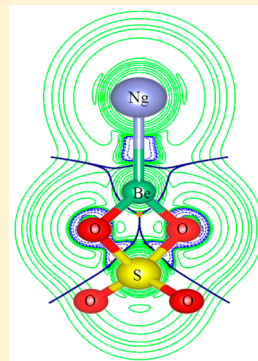
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S Supporting Information

ABSTRACT: Ab initio computations are carried out to assess the noble gas (Ng) binding capability of BeSO₄ cluster. We have further compared the stability of NgBeSO₄ with that of the recently detected NgBeCO₃ cluster. The Ng–Be bond in NgBeCO₃ is somewhat weaker than that in NgBeO cluster. In NgBeSO₄, the Ng–Be bond is found to be stronger compared with not only the Ng–Be bond in NgBeCO₃ but also that in NgBeO, except the He case. The Ar–Rn-bound BeSO₄ analogues are viable even at room temperature. The Wiberg bond indices of Be–Ng bonds and the degree of electron transfer from Ng to Be are somewhat larger in NgBeSO₄ than those in NgBeCO₃ and NgBeO. Electron density and energy decomposition analyses are performed in search of the nature of interaction in the Be–Ng bond in NgBeSO₄. The orbital energy term (ΔE^{orb}) contributes the maximum (ca. 80–90%) to the total attraction energy. The Ar/Kr/Xe/Rn–Be bonds in NgBeSO₄ could be of partial covalent type with a gradual increase in covalency along Ar to Rn.



■ INTRODUCTION

Ramsay and Rayleigh¹ discovered argon as the first noble gas (Ng) element in 1894. After this, the rest of the noble gases were discovered within 3 years.^{2,3} The Ng atoms have completely filled valence orbitals so that they become chemically inactive toward other chemical entities. For a long period of time after their discovery, Ng atoms are thought to be unable to form chemical compounds, and they were considered as inert elements. The myth on the inertness of Ng was broken after synthesis of Xe⁺(PtF₆)[−] by Bartlett^{4,5} in 1962. In the same year, Hoppe and his group⁶ reported the synthesis of XeF₂ in crystalline form. The syntheses of XeF₄, RnF₂, and KrF₂ were also reported in a very short interval.^{7–9} These pioneering works provided momentum toward the search for new Ng compounds. Consequently, a large number of Ng compounds were synthesized by the experimentalists^{10–14} or were predicted in silico by the theoreticians.^{15–25}

The theoretical studies reveal that metal ions with positive charge and small size like Li^{26–29} and Be^{26,30} have high polarizing ability to deform the electron density on Ng and thereby are good candidates in forming a chemical bond with them. Many theoretical investigations on the Ng–Be interaction were studied in NgBeY^{30–36} (Y = O, S, Se, Te, NH, CO₃) type of compounds. The Ng binding ability of the Be center was governed by the electronegativity of Y. In NgBeY molecule, the interaction between Ng and Be is of donor–acceptor type. The positively charged Be center is capable of accepting the electron density from Ng atom. Theoretical studies show that BeO molecule can be able to form compound even with the smallest He, and the He–Be bond has the dissociation energy of ~3 kcal/mol.³⁷ The electron-accepting

ability of Be and, hence the Be–Ng bond strength can be modified by changing the ligand bound to the Be center. Grandinetti et al.³⁸ attached BeO with a Lewis acid (BH₃) and substituted H atom of BeNH with different groups,³⁵ which indeed improve the Ng binding ability of the Be center; however, BeO–BH₃ and BeN–R are not global minima, rather the global minima are the ones that have Be center in between two atoms. Therefore, they can no longer bind Ng atoms effectively. Recently, we reported linear BeN–CN and BeN–BO clusters as their global minima structures, which have enhanced Ng binding ability compared with those of BeNH and BeO.³⁹ Some Be-containing clusters, in which Be is linked to electronegative N atoms like CN₃Be₃⁺, Be₂N₂, Be₃N₂, and BeSiN₂, were also found to bind Ng atoms quite effectively.^{33,40} Very recently Zhou, Frenking, and coworkers³⁴ performed both experimental and theoretical studies on NgBeCO₃ and NgBeO clusters (Ng = He–Rn) and found that the Ng–Be interaction in NgBeCO₃ is somewhat weaker than that in NgBeO. Here in this work we have presented a comparative study on the stability of NgBeSO₄, NgBeCO₃ and NgBeO clusters (Ng = He–Rn). The Ng–Be bond dissociation energy, dissociation enthalpies, and Gibbs' free-energy changes for the dissociation process are computed for each compound. Calculation shows that the Ng–Be interaction in NgBeSO₄ is stronger than those in NgBeCO₃ and NgBeO (except for the case of HeBeO). The natural bond orbital (NBO), electron density, and energy

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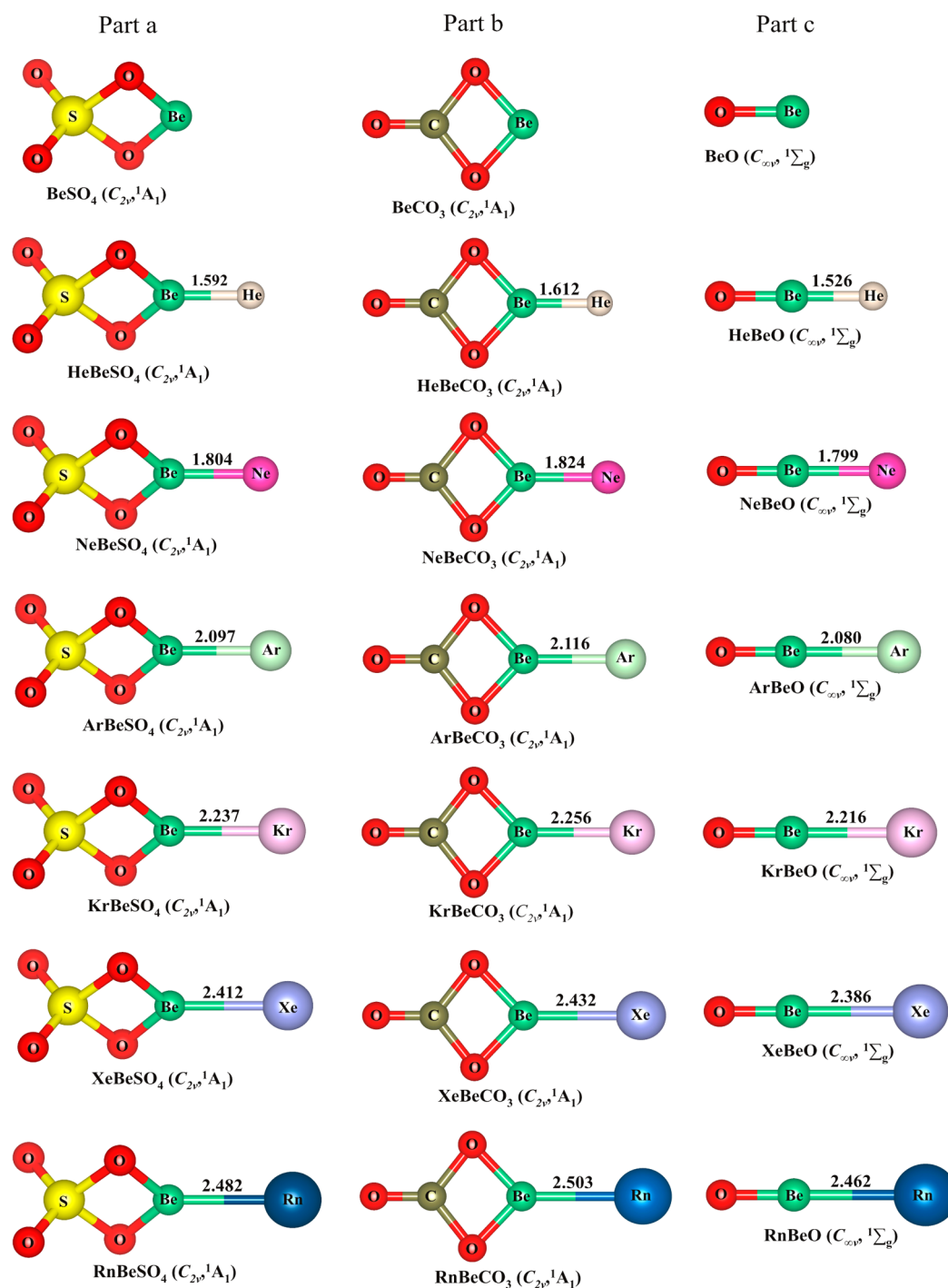


Figure 1. Optimized structures of NgBeY ($\text{Ng} = \text{He}, \text{Ne}, \text{Ar}, \text{Kr}, \text{Xe}, \text{and Rn}$ and $\text{Y} = \text{SO}_4, \text{CO}_3, \text{and O}$) at the MP2/def2-QZVPPD level. (The point group and the electronic state of the molecule are given in parentheses, and the Ng–Be bond lengths are in angstroms (Å).)

decomposition analyses (EDAs) are carried out for NgBeSO_4 clusters to understand the nature of bonding in Be–Ng bond.

COMPUTATIONAL DETAILS

The geometrical structures of the investigated systems are optimized at the MP2⁴¹/def2-QZVPPD⁴² and CCSD(T)⁴³/def2-TZVP⁴² levels with Gaussian 09 program package.⁴⁴ The effective core potential is used for the core electrons of Xe and Rn.⁴⁵ The frequency calculations are also carried out at MP2/def2-QZVPPD level of theory to assess the nature of the stationary state of the optimized geometry and to make zero-

point energy (ZPE) corrections. The electronic charges on each atom of the molecule and Wiberg bond index (WBI)⁴⁶ are computed by NBO analysis at the same level. The topological analysis of the electron density⁴⁷ is carried out at the MP2/def2-QZVPPD/WTBS level by using Multiwfn software.⁴⁸ All-electron WTBS basis set is used for Xe and Rn atoms. The EDA^{49–52} is carried out using ADF(2013.01) program package⁵³ at the PBE-D3⁵⁴/TZ2P⁵⁵/MP2/def2-QZVPPD level. Scalar relativistic effects are considered for the heavier atoms using the zeroth-order regular approximation (ZORA). The correction of basis-set superposition error (BSSE) is done

Table 1. BSSE- and ZPE-Corrected Dissociation Energy (D_0^{BSSE} , kcal/mol), Dissociation Enthalpy (ΔH , kcal/mol), and Free-Energy Change (ΔG , kcal/mol) at 298 K for the Dissociation Process: $\text{NgBeY} \rightarrow \text{Ng} + \text{BeY}$, NPA Charges at Be and Ng Centers (q , au), Wiberg Bond Indices of Be–Ng Bonds (WBI), and Be–Ng Bond Distances ($r(\text{Be–Ng})$, Å) of NgBeY Compounds Computed at the MP2/def2-QZVPPD Level^b

clusters	PG	D_0^{BSSE}	$D^{\text{CCSD(T)}\alpha}$	ΔH	ΔG	q_{Ng}	q_{Be}	WBI	$r(\text{Be–Ng})$
BeSO ₄	C _{2v}						1.51		
HeBeSO ₄	C _{2v}	2.7	3.3	3.3	−3.8	0.10	1.36	0.19	1.592
NeBeSO ₄	C _{2v}	4.1	4.6	4.9	−2.3	0.08	1.40	0.16	1.804
ArBeSO ₄	C _{2v}	10.4	11.5	11.2	3.9	0.21	1.25	0.37	2.097
KrBeSO ₄	C _{2v}	12.2	13.6	13.4	6.2	0.25	1.21	0.44	2.237
XeBeSO ₄	C _{2v}	14.6	15.8	16.1	9.0	0.31	1.16	0.53	2.412
RnBeSO ₄	C _{2v}	15.5	17.9	17.8	10.7	0.32	1.15	0.55	2.482
BeCO ₃	C _{2v}						1.49		
HeBeCO ₃	C _{2v}	2.1	2.7	2.7	−4.0	0.10	1.36	0.18	1.612
NeBeCO ₃	C _{2v}	3.4	3.9	4.1	−2.6	0.08	1.39	0.15	1.824
ArBeCO ₃	C _{2v}	8.9	10.0	9.7	2.9	0.19	1.26	0.35	2.116
KrBeCO ₃	C _{2v}	10.5	11.8	11.6	4.9	0.24	1.22	0.42	2.256
XeBeCO ₃	C _{2v}	12.6	13.8	14.0	7.4	0.28	1.17	0.49	2.432
RnBeCO ₃	C _{2v}	13.4	15.7	15.6	9.0	0.30	1.16	0.51	2.503
BeO	C _{∞v}						1.40		
HeBeO	C _{∞v}	3.5	3.6	4.3	−2.4	0.09	1.23	0.17	1.526
NeBeO	C _{∞v}	3.6	3.6	4.5	−2.2	0.07	1.29	0.13	1.799
ArBeO	C _{∞v}	10.0	10.6	10.8	4.2	0.17	1.15	0.32	2.080
KrBeO	C _{∞v}	11.8	12.8	13.0	6.4	0.22	1.11	0.39	2.216
XeBeO	C _{∞v}	14.3	15.3	15.7	9.3	0.27	1.05	0.47	2.386
RnBeO	C _{∞v}	15.1	17.4	17.2	10.7	0.28	1.05	0.49	2.462

^a $D^{\text{CCSD(T)}}$ is the ZPE-uncorrected dissociation energy at the CCSD(T)/def2-TZVP level. ^bNg = He–Rn; Y = SO₄, CO₃, O.

by employing the standard counterpoise (CP) method of Boys and Bernardi.⁵⁶

RESULTS AND DISCUSSION

The optimized geometries of all NgBeY clusters (Ng = He–Rn; Y = O, CO₃, SO₄) are provided in Figure 1. The geometries of NgBeSO₄ and NgBeCO₃ correspond to C_{2v} symmetry and ¹A₁ electronic state, whereas that of NgBeO belongs to C_{∞v} point group and ¹Σ_g electronic state. The related results are tabulated in Table 1. The ZPE- and BSSE-corrected bond dissociation energy (D_0^{BSSE}) for the dissociation of Ng–Be bond increases in going from He to Rn in all cases, as expected from their gradual increase in polarizability. The comparative study between NgBeSO₄ and NgBeCO₃ discloses that the D_0^{BSSE} values of the Ng–Be bonds somewhat improve in the former cases compared with the latter ones. The improvement in D_0^{BSSE} is 0.6 kcal/mol for He, 0.7 kcal/mol for Ne, 1.5 kcal/mol for Ar, 1.7 kcal/mol for Kr, 2.0 kcal/mol for Xe, and 2.1 kcal/mol for Rn. Even NgBeSO₄ possesses somewhat higher D_0^{BSSE} value than that in NgBeO, except the He case. The D_0^{BSSE} value of the He–Be bond in HeBeO is found to be 0.8 kcal/mol higher than that of the He–Be bond in HeBeSO₄, but for the rest of the Ng atoms the corresponding D_0^{BSSE} values in NgBeSO₄ are found to increase slightly (around 0.3 to 0.5 kcal/mol) compared with those of Ng–Be bonds in NgBeO. Thus, the Ng-binding ability of BeSO₄ (except He) is better than those of BeCO₃ and BeO. A further investigation on the NgBeY clusters (Ng = He–Rn; Y = O, CO₃, SO₄) at the CCSD(T)/def2-TZVP level also shows somewhat similar trends.

The stability of these NgBeY clusters with respect to the dissociation into Ng and BeY could be further understood from the dissociation enthalpy (ΔH) and Gibbs' free-energy change (ΔG) values for the dissociation processes, calculated at the

MP2/def2-QZVPPD level. In all cases, the dissociation processes are endothermic in nature with gradual increment along He to Rn. It may be noted that similar to the D_0 values, ΔH values follow the order $\Delta H(\text{NgBeSO}_4) > \Delta H(\text{NgBeO}) > \Delta H(\text{NgBeCO}_3)$, except for the He case. For such type of dissociation processes, ΔS is positive, hence a favorable term. At 298 K, the dissociation processes for Ar–Rn bound BeY clusters are found to be endergonic in nature; however, for He- and Ne-bound analogues, the dissociation processes are thermochemically spontaneous at room temperature. A lower temperature is required for them to make the favorable $T\Delta S$ term less important. Note that the dissociation of NgBeSO₄ into Ng and BeSO₄ is more endergonic in nature than that of NgBeCO₃; however, the same is slightly less endergonic (ranging 0.0 to 0.3 kcal/mol) than that of NgBeO.

The Ng–Be bond-stretching frequencies and their corresponding IR intensities in NgBeSO₄ clusters are provided in the Supporting Information. (See Table S1 in Supporting Information.) The Ng–Be stretching frequencies follow a decreasing order within the range of 120–315 cm^{−1} in moving from He to Rn. On the contrary, the respective stretching modes show negligible IR intensities.

To know the nature of Ng–Be bond, we have performed natural population analysis (NPA), WBI calculation, electron density analysis, and EDA for these Ng compounds. The NPA charges show that there are positive charges on the Ng atoms. This indicates some degree of electron transfer from Ng atoms to the BeY moiety. The electron transfer is the least in Ne case, but it gradually increases in moving from Ar to Rn (Table 1). For a given Ng atom, the degree of electron transfer from Ng to Be center follows the order: NgBeSO₄ > NgBeCO₃ > NgBeO. It is related to the positive charge on the Be center. Because the positive charge on the Be center in BeSO₄ (+1.51|e|) is larger than those on the Be centers in BeCO₃ and BeO, it could

Table 2. Electron Density Descriptors (au) at the Bond Critical Points (BCPs) of Ng–Be Bond in NgBeSO₄ Obtained from the Wave Functions Generated at the MP2/def2-QZVPPD Level^a

clusters	$\rho(r_c)$	$\nabla^2\rho(r_c)$	$G(r_c)$	$V(r_c)$	$H(r_c)$	$r(\text{Be–Ng})$	r_{cov}
HeBeSO ₄	0.022	0.242	0.049	−0.037	0.012	1.59	1.24
NeBeSO ₄	0.023	0.257	0.053	−0.042	0.011	1.80	1.54
ArBeSO ₄	0.031	0.209	0.049	−0.046	0.003	2.10	2.02
KrBeSO ₄	0.031	0.169	0.043	−0.043	−0.001	2.24	2.12
XeBeSO ₄	0.035	0.145	0.043	−0.050	−0.001	2.41	2.36
RnBeSO ₄	0.031	0.111	0.034	−0.039	−0.001	2.48	2.46

^a r_{cov} is covalent bond distances taken from ref 62.

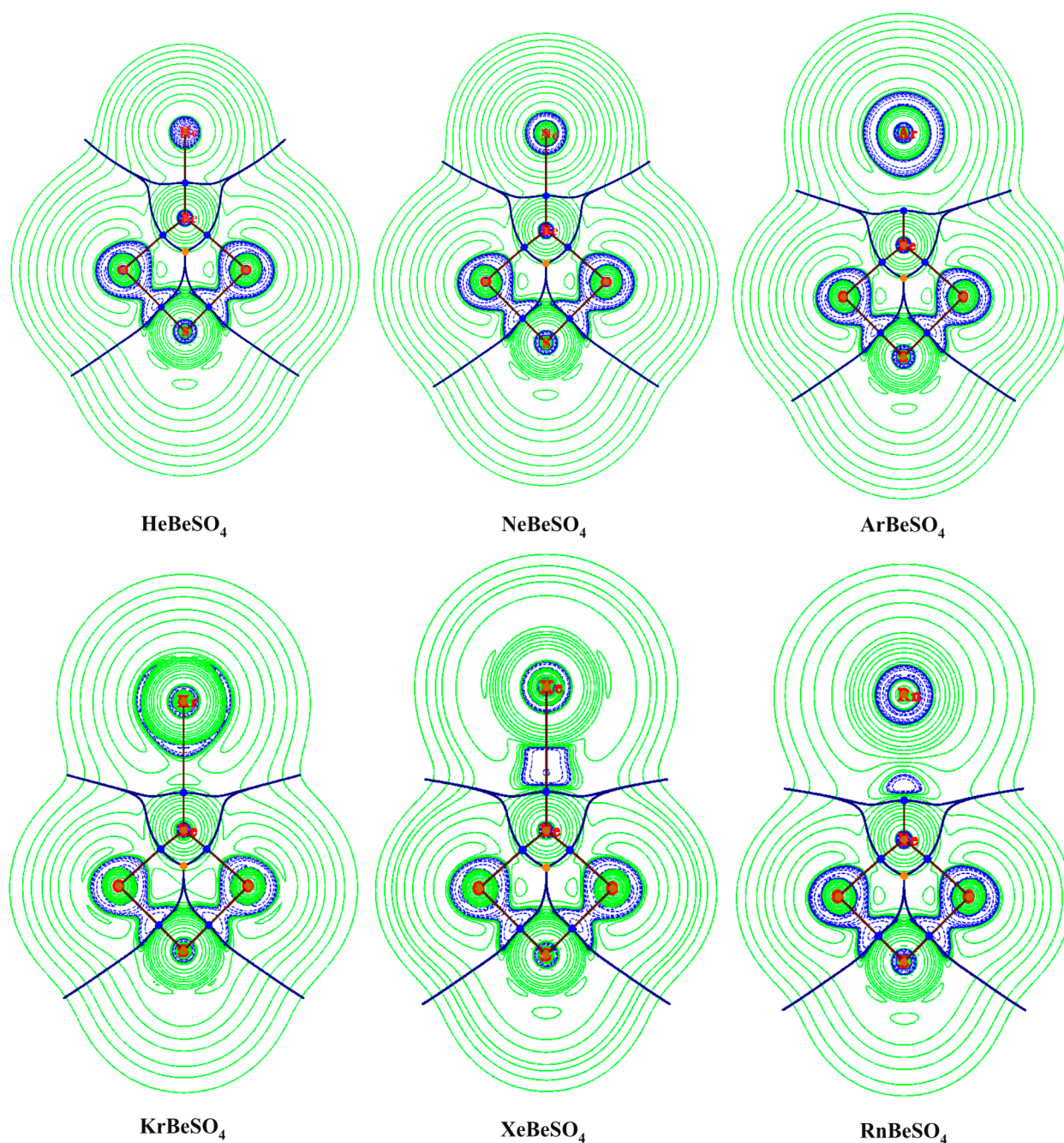


Figure 2. Contour diagrams of the Laplacian of the electron density of NgBeSO₄ (Ng = He–Rn) at Ng–Be–O–S plane at the MP2/def2-QZVPPD level. (Green solid lines stand for $\nabla^2\rho(r) > 0$, whereas blue-dashed lines stand for $\nabla^2\rho(r) < 0$.)

polarize the electron density of the Ng atoms more, resulting in a somewhat larger electron transfer from Ng to Be. The WBI

values show the degree of covalency in the Ng–Be bond. A small value of WBI indicates noncovalent (van der Waals or

Table 3. Energy Decomposition Analysis of NgBeSO₄ Clusters Taking Ng As One Fragment and BeSO₄ As Another at the PBE-D3/TZ2P//MP2/def2-QZVPPD Level^{a,b}

clusters	ΔE^{Pauli}	ΔE^{elstat}	ΔE^{orb}	ΔE^{dis}	ΔE^{int}
HeBeSO ₄	6.4	−1.0(8.8%)	−9.6(88.8%)	−0.3(2.4%)	−4.5
NeBeSO ₄	8.2	−2.3(16.9%)	−10.9(80.5%)	−0.4(2.7%)	−5.3
ArBeSO ₄	13.1	−2.7(11.0%)	−21.4(86.4%)	−0.6(2.5%)	−11.6
KrBeSO ₄	14.0	−2.6(9.3%)	−24.7(88.0%)	−0.8(2.7%)	−14.1
XeBeSO ₄	15.0	−2.4(7.4%)	−28.5(89.9%)	−0.9(2.7%)	−16.7
RnBeSO ₄	15.7	−2.2(6.6%)	−30.1(90.4%)	−1.0(3.0%)	−17.5

^aPercentage in parentheses is the contribution of each term toward the total attraction ($\Delta E^{\text{elstat}} + \Delta E^{\text{orb}} + \Delta E^{\text{dis}}$). ^bAll energy terms are in kcal/mol.

electrostatic) type of interaction, whereas a high WBI value indicates the covalent character. In our case, WBI value of Be–Ng bond is low for He and Ne cases, but it becomes gradually larger along Ar to Rn. In fact, for Kr–Rn, almost half a bond order occurs between Be and Ng atoms. It may also be noted that for a particular Be–Ng bond, WBI value is somewhat larger in NgBeSO₄ than those in BeCO₃ and BeO.

It may be noted that although the calculated Be–Ng bond distances in NgBeSO₄ are slightly longer than those in NgBeO, the computed D_0^{BSSE} values in the former cases are somewhat larger than those in latter cases. In a recent paper, Frenking and coworkers⁵⁷ argued that the equilibrium bond distance is decided by the Pauli repulsion term (ΔE^{Pauli}). A bond avoids further shortening, when the attractive orbital (ΔE^{orb}) and electrostatic (ΔE^{elstat}) terms cannot compensate the increase in repulsive ΔE^{Pauli} term. Because of the different ligands attached with the Be center, the positive charges on the Be centers of BeSO₄ and BeO are different. Consequently, ΔE^{Pauli} as well as other contributing terms originated in the Be–Ng bonds are different in the two compounds. We have carried out EDA by imposing the Kr–Be bond distance in KrBeSO₄ as that in KrBeO. (See Table S2 in Supporting Information.) As obvious from the result, further shortening from the equilibrium geometry increases the interaction energy (ΔE^{int}) by 0.1 kcal/mol. The ΔE^{int} represents the instantaneous difference between the energy of Ng-bound complex and the sum of the energies of fragments having the constrained geometries as that in the Ng-bound complex. Although attractive ΔE^{orb} and ΔE^{elstat} terms also increase upon compression, the repulsive ΔE^{Pauli} term increases more to induce overall instability by 0.1 kcal/mol on the system. It may be further noted that a similar type of results is obtained in a previous paper also.³⁹

Several parameters at the bond critical point (BCP) of Ng–Be bond in NgBeSO₄ clusters are calculated to understand the nature of interaction between Ng and Be atoms. (See Table 2.) The negative and positive values of the Laplacian of electron density ($\nabla^2\rho(r_c)$) indicate concentration and depletion of electron density ($\rho(r_c)$) at BCP, respectively. According to general topological criterion, a covalent bond has negative $\nabla^2\rho(r_c)$ at BCP, but in many cases like the systems with heavier atom^{58–60} and some covalent compounds like F₂ and CO,⁴⁷ this criterion fails to explain the covalent bonding character. Then, other parameters such as local kinetic energy density ($G(r_c)$), local potential energy density ($V(r_c)$), and local total energy density ($H(r_c)$; $H(r_c) = G(r_c) + V(r_c)$), are used to describe the bonding situation. Cremer and coworkers⁶¹ proposed that a bond might be considered as partial covalent type even if $H(r_c)$ is less than zero. In all our cases, $\nabla^2\rho(r_c)$ is found to be positive, whereas for Kr–Rn cases, $H(r_c)$ is negative. Therefore, Kr/Xe/Rn–Be bonds might be treated as of partial covalent bond type. We have also provided in Table 2

the typical covalent bond distances of Be–Ng bonds as reported by Cordero et al.⁶² The Be–Ng bond distance is found to be only 0.08 Å for Ar, 0.12 Å for Kr, 0.05 Å for Xe, and 0.02 Å for Rn larger than those of the corresponding typical covalent bond distances. Note that although topological descriptors describe Ar–Be bond as of noncovalent type, the Ar–Be bond distance is quite closed to that of covalent bond distance and the WBI value is also ~0.4. Therefore, it would be better to consider this bond as of partial covalent type, and of course the degree of covalency increases in moving from Ar to Rn. The contour plots of the Laplacian of the electron density are displayed in Figure 2. In the plots, the solid green lines show the region with $\nabla^2\rho(r) > 0$, whereas the dotted blue lines highlight the region with $\nabla^2\rho(r) < 0$. In moving from He to Rn, the shape of the valence orbitals gets deformed with gradual increase and finally a well-defined region with $\nabla^2\rho(r) < 0$, as shown by the dotted blue color being developed in cases of Be–Xe and Be–Rn bonds.

The results from EDA provide more insight into the nature of bonding. Here the EDA is performed at the PBE-D3/TZ2P//MP2/def2-QZVPPD level, taking Ng as one fragment and BeSO₄ as another (Table 3). The negative and positive values for the energies correspond to the attractive and repulsive nature of the interaction, respectively. Among all attractive terms, the contribution from the ΔE^{orb} is found to be the maximum toward the total attraction energy (ca. 80–90%). The contribution from the ΔE^{elstat} is only around 6–17% of the total attraction energy, whereas the dispersion (ΔE^{dis}) term is not at all important, as it contributes the least (ca. 2 to 3%). Note that the magnitude of the ΔE^{orb} term gradually becomes larger in moving from He to Rn, implying an increase in covalent character along the same.

CONCLUSIONS

The geometry of NgBeSO₄ is found to have a C_{2v} symmetry and ¹A₁ electronic state. The D_0^{BSSE} value of the Ng–Be bond for NgBeSO₄ is somewhat larger than those of the corresponding Ng–Be bonds in NgBeCO₃ and NgBeO, except the HeBeO case. Consequently, the dissociation of NgBeSO₄ into Ng and BeSO₄ is more endothermic in nature compared with those in the corresponding NgBeCO₃ and NgBeO clusters. The Ar–Rn bound analogues are found to be viable even at 298 K. The dissociation of NgBeSO₄ into Ng (Ng = Ar–Rn) and BeSO₄ is more endergonic in nature than that of NgBeCO₃ but slightly less endergonic (ranging from 0.0 to 0.3 kcal/mol) than that of NgBeO. The CCSD(T) results corroborate well with the results obtained at the MP2 level. Owing to higher positive charge at Be center, the electron transfer from Ng to Be is larger in NgBeSO₄ than those in NgBeCO₃ and NgBeO. The WBI values of Ng–Be bonds show that almost half a covalent bond is formed in Kr–Rn-bound

BeSO₄ analogues. Electron density analysis indicates that Kr/Xe/Rn–Be bond can be categorized as of partial covalent type. The ΔE^{orb} is the maximum contributor toward the total attraction energy (ca. 80–90%). For Ar–Rn-bound analogues, the magnitude of ΔE^{orb} is quite high, which gradually becomes larger along Ar to Rn, implying larger covalent character along the same. Although $H(r_c)$ is slightly positive for Ar–Be bond in ArBeSO₄, the WBI value is ~ 0.4 and the bond length is only 0.08 Å larger than that of typical Ar–Be covalent bond. Furthermore, the ΔE^{orb} value for this bond is also quite high (–21.4 kcal/mol). Therefore, we have categorized it as of partial covalent type.

■ ASSOCIATED CONTENT

■ Supporting Information

Calculated vibrational stretching frequencies and their IR intensities for Ng–Be bond of NgBeSO₄ and the energy decomposition analysis of KrBeSO₄ cluster. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.5b03888.

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Notes

The authors declare no competing financial interest.

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