

알칼리 금속-비활성 기체 반데르발스 복합체에 대한 양자화학적 계산

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ab initio Calculations on Alkali Atom - Rare Gas Van Der Waals Clusters

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요 약. $M\text{-Rg}$ 및 $M\text{-Rg}_2$ ($M=\text{Li}, \text{Na}, \text{Rg}=\text{He}, \text{Ar}$) 반데르발스 복합체들에 대한 양자화학적 계산을 시행하였다. All-electron MP2(6-311++G(3df, 3pd))에 의하여 계산된 LiHe , LiAr 및 NaAr 의 균형 핵간 거리와 결합 에너지는 실험값과 잘 일치하였다. LiHe_2 , LiAr_2 및 NaAr_2 에 대하여 계산된 분광학적 성질들도 또한 계산하였다.

ABSTRACT. *ab initio* calculations are presented for $M\text{-Rg}$ and $M\text{-Rg}_2$ ($M=\text{Li}, \text{Na}, \text{Rg}=\text{He}, \text{Ar}$) van der Waals clusters. Internuclear distances and binding energies of LiHe , LiAr and NaAr obtained by all-electron MP2(6-311++G(3df, 3pd)) method are in good agreement with experimental values. Calculated properties of LiHe_2 , LiAr_2 , NaHe_2 and NaAr_2 are also reported.

Van der Waals clusters have attracted considerable attention both experimentally¹⁻⁵ and theoretically⁶⁻⁸ for a long time. Progress in molecular beam technology allowed large amounts of information on the structure and reactivity to be accumulated for various kinds of van der Waals clusters. Alkali metal-rare gas clusters are the simplest and prototypical example. Besides their importance in understanding the long range interactions, they began to be investigated as a good example for spin-orbit changing collision experiments.⁹ Theoretically, it has long been considered to be rather difficult to investigate the alkali metal-rare gas system by *ab initio* methods due to the long range nature of the interactions between atoms. Since the binding energy is usually less than 50 cm⁻¹ for these systems, Hartree-Fock level of theory will certainly not be adequate. Some full CI calculations⁶ were carried out to give the geometry and binding energies, which are in good agreement with experiments on

alkali metal - rare gas diatomics, but will probably be too expensive to perform for polyatomics. A computation based on simulated annealing⁸ was tried for polyatomic alkali metal-rare gas systems, but the geometry obtained was only in partial agreement with experiments. In order to calculate the properties of the van der Waals system, such important factors as the long range dispersion forces and electron correlation should properly be incorporated in quantum chemical calculations.

In this work, we employ all electron Moeller-Plesset (MP) methods to obtain the structures of the smaller alkali metal-rare gas van der Waals systems, and to analyze the appropriateness of the methods and the basis sets employed. GAUSSIAN 94 suite of programs¹⁰ were used to carry out the calculations. We compute the equilibrium structures and binding energies. The calculated results are compared with experiments and other theoretical calculations. We find that the all-electron MP2

Table 1. Bond length and binding energy of NaAr obtained by HF and all-electron MP2 methods

	Bond Length (Å)	Binding Energy (cm ⁻¹)
HF (6-311+G**)	7.90	0.77
HF(6-311++G(3df, 3pd))	7.60	0.90
MP2 (6-311+G**)	6.29	12.58
MP2 (6-311++G(3df, 3pd))	5.13	45.43

calculations with large basis (6-311++G(3df, 3pd)) are needed to obtain the molecular parameters that are in good agreement with experiments.

Table 1 presents equilibrium bond length and binding energy of NaAr obtained by Hartree-Fock and MP2 level of theory. Two basis sets, 6-311+G** and 6-311++G(3df, 3pd), are employed for both methods. It can be seen that the Hartree-Fock level of theory with large basis sets available in Gaussian 94 gives bond length and binding energy that are in complete disagreement with experimental results. The binding energy is found to almost vanish, while the experimental value is about 40 cm⁻¹. It should be noticed that even the bond length (7.6 Å) obtained by Hartree-Fock calculations is very different from the experimental one (about 5 Å) by more than 2 Å. Considering that the Hartree-Fock theory usually gives fairly accurate bond lengths in many molecules, it indicates that alkali metal-rare gas van der Waals system is indeed a very tricky molecule to treat theoretically. This is further verified in the MP2 calculations. The all-electron MP2 calculations with pretty large basis 6-311+G** also result in poor bond length and binding energy (frozen core MP2 method would give results identical to the Hartree-Fock calculations, since NaAr has only one valence electron). Changing the basis from 6-311+G** to 6-311++G(3df, 3pd), however, leads to dramatic changes as presented in *Table 1*. The bond length and the binding energy are obtained to be 5.13 Å and 45.43 cm⁻¹, respectively. The difference between the calculations employing the two basis sets is also presented in *Table 2*, where the energies are given near the minimum energy configurations. These values agree very well with experimental values as shown in *Table 3*. The bond lengths obtained by all electron MP2 method using 6-311++G(3df, 3pd) basis in the present calculations (5.13 Å) are close to the experimental value^{11,12} (about 5 Å). *Table 3* also pre-

Table 2. Energy of NaAr calculated by all electron MP2 method using two basis sets (6-311+G** and 6-311++G(3df, 3pd))

R (Å)	MP2 (6-311+G**)	MP2 (6-311++G(3df, 3pd))
4.5	-688.9856779	-689.1092731
4.9	-688.9859082	-689.1093713
5.0	-688.9859421	-689.1093099
5.1321	-----	-689.1093817*
5.2	-688.9859912	-689.1093786
5.3	-688.9860092	-689.1093778
5.4	-688.9860232	-689.1093726
5.6	-688.9860428	-689.1093583
5.7	-688.9860493	-689.1093499
5.8	-688.9860543	-689.1093411
6.0	-688.9860603	-689.1093232
6.1	-688.9860619	-689.1093144
6.2	-688.9860628	-689.1093058
6.2898	-688.9860630*	-----
6.5	-688.9860622	-689.1092819
6.9	-688.9860574	-689.1092556
∞	-688.9860150	-689.1091747

*Minimum energy point

Table 3. Bond lengths and binding energies of M-Ar (M=Li, Na)

	Bond length (Å)	Binding Energy (cm ⁻¹)
LiAr		
theoretical(MP2)	5.08 (1)	36.98 (1)
experimental	4.95 (2)	42.8 (2)
	4.89 (3)	42.5 (3)
NaAr		
theoretical(MP2)	5.13 (1)	45.43 (1)
mixed quantum/classical	5.59 (4)	56.8 (4)
experimental	4.81 (5)	42 (5)
	4.99 (6)	39 (6)
	5.01 (2)	45 (2)

(1) Present work (all electron MP2/6-311++G(3df, 3pd)).

(2) Ref. 12 (3) Ref. 13 (4) Ref. 8(a) (5) Ref. 11 (6) Ref. 1.

sents similarly calculated results obtained for LiAr by employing all-electron MP2 method with 6-311++G(3df, 3pd) basis. The potential curves of the alkali metal-rare gas diatomics would be very useful to simulate the experiments on the alkali metal impurity in rare gas matrix¹⁴⁻¹⁷ that motivated the present work, since they may be employed as pairwise potentials between the alkali metal and rare gas atoms.

Due to the small polarizability of the He atom, the

Table 4. Bond lengths and binding energies of M-He (M=Li, Na)

	Bond length (Å)	Binding Energy (cm ⁻¹)
LiHe		
Theoretical(MP2)	6.10(1)	1.95(1)
experimental	6.03(2)	1.14(2)
	6.20(3)	1.34(3)
NaHe		
	6.10(1)	2.54(1)
	6.41(3)	1.20(3)

(1) Present work (all electron MP2/6-311++G(3df, 3pd))
 (2) Ref. 18. (3) Ref. 7.

bonding in metal - helium clusters are expected to be extremely weak. The bond distances of alkali metal - helium atom are known to be very large (about 6 Å), and the binding energies are essentially nonexistent (about 1 cm⁻¹, see Table 4). Our calculations also verify these extremely weak bonding, as presented in Table 4. The calculated bond lengths of LiHe and NaHe (6.19 and 6.22 Å, respectively) are larger than the corresponding metal-argon complexes by a little more than 1 Å, indicating weaker bonding in the metal complexes with helium atom. Agreement with experiment¹⁸ (for LiHe) and other theoretical results⁷ (for NaHe) is very good. It should be added that the Hartree-Fock calculations employing the same large basis would give considerably larger bond distances⁵ for these diatomic clusters (by 2.47 Å for the case of NaAr). One possible source of inaccuracy in the *ab initio* computations for the binding energies of the very weakly bound van der Waals clusters may be due to the basis set superposition errors (BSSE). Since the binding energies reported above are rather small (less than 50 cm⁻¹), they may be prone to such errors, especially for NaHe and LiHe compounds. Since the correction procedures of the BSSE are quite arbitrary, however, and since the BSSE tends to get smaller when using larger basis set, we did not attempt to consider the BSSE here.

For polyatomic alkali metal-rare gas van der Waals clusters, there exists very little information. Simulated annealing calculations by Singer and coworkers⁸ seem to be the only work on these very interesting systems. Due to the difficulty of size-selecting the neutral clusters, no experimental data are available yet. We employ all-elec-

tron MP2 method to compute the structure of the smallest polyatomic alkali metal-rare gas van der Waals clusters, that is, NaAr₂, LiAr₂, NaHe₂ and LiHe₂. In a theoretical work, Singer and coworkers found^{8(a)} that the cluster is highly bent, with the Na-Ar distance of 5.4-5.5 Å. We find in the present calculations (see Table 5) carried out under C_{2v} symmetry constraint that the Na-Ar distance and the bond angle are 5.15 Å and 43 degrees, respectively (The Hartree - Fock optimized values are 7.43 Å and 40 degrees). Since the bond length of NaAr presented in this work is in good agreement with experiment, we believe that the bond length of 5.15 Å obtained in the present calculations is close to the real bond length of NaAr₂. The cluster seems to be very floppy, since the vibrational quantum for bending mode is found to be very small (10.3 cm⁻¹). The distance between the two argon atoms in NaAr₂ is 3.5 Å. Since the bond length of Ar₂ is 4.82 Å, the distance between the two argon atoms in NaAr₂ is significantly shorter. This indicates that the sodium atom acts to increase the bonding of the two argon atoms in NaAr₂. This three-body interaction in NaAr₂ is also seen in the binding energy, which is obtained as the difference between the energy at the optimized geometry and that of the fully dissociated system (a sodium atom and two argon atoms). The binding energy of NaAr₂ obtained in the present calculations is 202.9 cm⁻¹, which is larger than the sum of the binding energies of pairwise interactions between a sodium atom and two argon atoms by about 30 cm⁻¹. This difference amounts to the contribution of the three-body interaction in NaAr₂. Table 5 presents the calculated properties of LiAr₂. The Ar-metal atom distance and the bond angle of LiAr₂ are very similar to those of NaAr₂.

Table 5 also presents the calculated properties of LiHe₂ and NaHe₂, for which no data are available for

Table 5. Calculated properties of M-Rg₂ (M=Li, Na, Rg=Ar, He)

	R _{M-Rg} (Å)	∠(Rg-M-Rg) (degree)	Binding energy (cm ⁻¹)
LiAr ₂	5.11	43.3	187.0
NaAr ₂	5.15	43.0	202.9
LiHe ₂	6.2	29.6	9.64
NaHe ₂	6.1	31.0	10.61

comparison. We find in the present calculations carried out under $C_{\infty v}$ symmetry constraint that LiHe_2 and NaHe_2 are highly bent, with bond angles of 29.6 and 31 degrees, respectively. The Li-He and Na-He distances in LiHe_2 and NaHe_2 are very similar to those in LiHe and NaHe , being 6.2 Å and 6.1 Å, respectively. Smaller bond angles of these triatomic clusters relative to those of M-Ar clusters (about 40 degrees) can be attributed to the smaller size of the helium atom. Binding energies of LiHe_2 and NaHe_2 are very small, being 9.6 cm^{-1} and 10.6 cm^{-1} , respectively. These binding energies are obtained as the energy difference between the optimized structures and the fully dissociated system (that is, a metal atom and two helium atoms). There may exist a small degree of three-body interactions that play to stabilize the LiHe_2 and NaHe_2 clusters as we have shown above for LiAr_2 and NaAr_2 . Since the magnitudes of the interactions are so small for the LiHe_2 and NaHe_2 clusters, however, they are not expected to stabilize the clusters in the present case to any significant degree. The small binding energies also indicate that the clusters will be extremely floppy. Although the vibrational frequencies of LiHe_2 and NaHe_2 could not be obtained in the present calculations, they are expected to be essentially vanishing. Considering all of these theoretical predictions, alkali metal-helium clusters will be observed only at extremely low temperatures. Our calculated results will hopefully stimulate further experiments on these very interesting van der Waals clusters. Larger clusters will be investigated in the near future.

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