

ON THE NATURE OF THE BONDING IN X-Be-O MOLECULES (X = He, Ne, Ar)

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Dedicated to Dr R. Zahradnik on the occasion of his 60th birthday.

The noble gas complexes, HeBeO, NeBeO, and ArBeO, discovered computationally by Koch and Frenking, were reexamined at various theoretical levels. The results depended strongly on the size of the basis set but were insensitive to electron correlation corrections. The MP2 association energies of BeO with the noble gases, obtained with extended basis sets, were 4.80, 4.76, and 10.12 kcal/mol, respectively. The surprising stability of HeBeO (compared to NeBeO) is due to greater charge-transfer from He to BeO (donation) as well as to charge-transfer in the reverse direction (back donation). This compensates for the larger induction energy due to the greater polarizability of neon. The basis set superposition error is very large with split-valence basis sets; improvement of *s* and *p* function descriptions strongly reduces but does not completely eliminate this error.

Complexes of the lighter noble gases generally are characterized by very low dissociation energies and large intersystem separations. Electron sharing between the noble gas and its partner is exceptional. Because of very high ionization potentials of the noble gases, such sharing can be expected to occur only with species possessing similarly high electron affinities.^{1,2} Indeed, pertinent to the present work, we have shown that Be²⁺ will bind up to six He, Ne, and Ar atoms quite strongly.³ Besides such charged species, the neutral BeO molecule was found computationally by Koch and Frenking¹ to be able to share electrons with noble gases.

This remarkable ability takes advantage of two characteristics. BeO is strongly polarized (the charge on Be is nearly 2+), and the lack of any screening electrons on beryllium allows the close approach of the noble gas atoms. The following noble gas-BeO association energies were calculated for HeBeO, NeBeO (MP4-SDTQ/6-311G (2*df*, 2*dp*)) and ArBeO (MP4SDTQ/6-311G*): 3.0, 2.5, 7.3 kcal/mol.^{1,2} However, the basis set superposition errors (BSSE) were 0.3, 5.6, and 4.9 kcal/mol, respectively. Since the BSSE for NeBeO is more than twice as large as the association energy, the quantitative accuracy of such results are suspect. Large BSSE values

(comparable to dissociation energies) clearly indicate⁴ basis set deficiencies. High values of BSSE for the X-BeO complexes (X = He, Ne, Ar) found by Koch and Frenking are not surprising because of the generally poor performance of split-valence basis sets for noble gases and molecular interactions.⁴ As a consequence, we have reinvestigated this problem; the most challenging question being the lower association energy of Ne-BeO in comparison to He-BeO. Is it artifact of the theoretical levels employed by Koch and Frenking or is it physical reality?

THEORETICAL

Basis set. A (8s) basis set contracted to [4s] (5111) was used for He;⁵ two sets of uncontracted *p*-functions with exponents⁵ 0.94151 and 0.218, and diffuse *d*-functions ($\alpha = 0.14$)⁶ were added. For Ne the (9s5p) basis set of Dunning and Hay was contracted to [3s2p] according to the recommended scheme,⁷ further [6s4p](4111112111) and [8s4p] (211111112111) basis sets were derived. One, two and three sets of *d*-functions and one set of diffuse *f*-functions with exponents 0.56; 0.28, 1.12; 0.19, 0.56, 1.68 (ref.⁸) and 0.28 (ref.⁹) were added. For Ar the (12s9p) basis set of McLean and Chandler was contracted to [6s5p] according to the recommended scheme;¹⁰ one, two and three sets of *d*-functions with exponents 0.28; 0.14, 0.56; and 0.009, 0.28, 0.84 were added.⁶ The diffuse *f*-functions had the same exponents as those of Ne. The exponents of polarization functions for He(*p,d*), Ne(*d,f*) and Ar(*d,f*) were optimized⁶ with respect either to the dispersion energy or to polarizability and are therefore much more diffuse than standard polarization functions. Diffuse polarization functions are necessary for proper estimation of polarizability of noble gases. With the present complexes, the induction energy between the highly charged BeO (nearly Be²⁺-O²⁻) and the neutral noble gases should be important.

For Be and O, the (9s5p) basis set was contracted to [3s2p]⁷ or to [6s4p] (4111112111). The polarization functions on these atoms were concentrated close to the nuclei (contrary to the diffuse function used at He, Ne, and Ar); the standard exponents were taken from Gaussian 82 (refs^{11,12}). When one and two sets of polarization functions the following exponents for Be and O were employed: 0.4; 0.2, 0.8; and 0.8; 0.4, 1.6.

Calculations. The stabilization energy of the noble gas-BeO complexes was determined using the MP2 method with the basis sets described in the previous section. The basis set superposition error was evaluated using the function counterpoise procedures of Boys and Bernardi.¹³ The starting geometries were taken from refs^{1,2} and reoptimized with respect to ΔE^{MP2} corrected for BSSE. The charge distribution and charge transfer energy was deduced from natural atomic orbital and natural bond orbital analysis of Reed and Weinhold.^{14,15} The energies of the isolated subsystems are collected in Table I.

RESULTS

HeBeO. Energy evaluations are summarized in Table II. The MP2 association energy obtained with our smallest basis set is complicated by an enormous BSSE. This originates in the poor description of BeO (see Table II). An even larger BSSE (23.7 kcal/mol) was obtained when the 6-31G* basis set was used for Be and O. Extending the *sp* functions on oxygen results in a sharp decrease of BSSE. This is not surprising since it is known: (i) that BSSE originates in the poor description of the innermost orbitals, and, (ii) that basis sets for anions and for first row atoms with lone pairs should be augmented by diffuse *s*- and *p*-functions. Further basis

TABLE I
HF and MP2 energies for He, Ne, Ar and BeO evaluated with different basis sets; energies in atomic units, 1 a.u. = 2 625.5 kJ/mol

System	$E(\text{HF})/E(\text{MP2})$			
He	<i>4s2p</i>	<i>4s2p1d</i>		
	-2.858877	-2.858877		
	-2.883930	-2.883948		
Ne	<i>3s2p1d</i>	<i>4s2p2d</i>	<i>6s4p2d</i>	<i>6s4p3d</i>
	-128.522483	-128.526518	-128.526879	-128.526518
	-128.644018	-128.691963	-128.730140	-128.751409
	<i>6s4p2d1f</i>	<i>8s4p1d</i>		
	-128.526518	-128.526741		
	-128.730001	-128.692229		
Ar	<i>6s5p1d</i>	<i>6s5p2d</i>	<i>6s5p3d</i>	<i>6s5p2d1f</i>
	-526.806626	-526.806626	-526.806626	-526.806626
	-526.896302	-526.954089	-526.975 35	-526.963484
BeO ^a	Be <i>3s2p1d</i>	<i>3s2p1d</i>	<i>3s2p1d</i>	<i>6s4p1d</i>
	O <i>3s2p1d</i>	<i>6s4p1d</i>	<i>9s5p1d</i>	<i>6s4p1d</i>
	-86.079506	-89.398967	-89.418777	-89.404402
	-86.236656	-89.656640	-89.676829	-89.662791
BeO ^a	Be <i>6s4p2d</i>	<i>6s4p2d1f</i>	<i>8s4p1d</i>	
	O <i>6s4p2d</i>	<i>6s4p2d1f</i>	<i>8s4p1d</i>	
	-89.406049	-89.407050	-89.421585	
	-89.686638	-89.707565	-89.680002	

^a $R = 13.47$ pm.

set extension results in only moderate increases of dissociation energy (cf. Table II); the BSSE is reduced, but even with the largest basis sets it is still significant. We reoptimized the geometry of HeBeO with the $4s2p(\text{He})$, $6s4p1d(\text{Be, O})$ basis sets; however, the changes were negligible.

NeBeO. Energy evaluations are collected in Table III. We first employed the geometry from refs^{1,2}. The BSSE with the smallest basis set again is enormous. As was the case with HeBeO, this is mainly due to the poor description of BeO. When the 6-31G* basis set was employed for Be and O, the BSSE is 23.1 kcal/mol. Increasing the quality of the oxygen basis set again results in a dramatic decrease in the BSSE; furthermore, the major BSSE contribution now involves neon.

TABLE II

HF and MP2 energies, MP2 stabilization energies (ΔE^{MP2}) and basis set superposition errors (BSSE) for HeBeO. Geometry taken from refs^{1,2}; He-Be 15.38 pm, Be-O 13.47 pm; energies in a.u. and kcal/mol, 1 a.u. = 2 625.5 kJ/mol, 1 kcal/mol = 4.184 kJ/mol

Quantity	Basis set		
	He $4s2p$ Be $3s2p1d$ O $3s2p1d$	$4s2p$ $3s2p1d$ $6s4p1d$	$4s2p$ $3s2p1d$ $9s5p1d$
$E(\text{HF})$	-89.032585	-92.269245	-92.289101
$E(\text{MP2})$	-89.242836	-92.552079	-92.572304
ΔE^{MP2}	-5.95	-4.63	-4.64
BSSE	19.23	2.59	2.60
BSSE ^a	0.13	0.12	0.12
BSSE ^b	19.10	2.47	2.48

Quantity	Basis set		
	He $4s2p1d$ Be $6s4p1d$ O $6s4p1d$	$4s2p1d$ $6s4p2d$ $6s4p2d$	$4s2p1d$ $6s4p2d1f$ $6s4p2d1f$
$E(\text{HF})$	-92.270669	-92.272190	-92.273186
$E(\text{MP2})$	-92.555270	-92.579041	-92.599875
ΔE^{MP2}	-4.72	-4.72	-4.80
BSSE	0.63	0.59	0.45
BSSE ^a	0.15	0.18	0.24
BSSE ^b	0.48	0.41	0.21

^a Deepening of the energy of He by the "ghost" orbitals of BeO; ^b deepening of the energy of BeO by the "ghost" orbitals of He.

TABLE III

HF and MP2 energies, MP2 stabilization energies (ΔE^{MP2}), and basis set superposition errors (BSSE) for NeBeO; energies in a.u. and kcal/mol, 1 a.u. = 2 625.5 kJ/mol, 1 kcal/mol = 4.184 kJ/mol

Quantity	Basis set ^d					
	Ne-4s2p1d	3s2p1d	6s4p2d	6s4p2d	6s4p2d	6s4p2d
Ne	3s2p1d					
Be	3s2p1d	3s2p1d	3s2p1d	6s4p1d	6s4p2d	6s4p2d
O	3s2p1d	6s4p1d	6s4p1d	6s4p1d	6s4p1d	6s4p2d
<i>E</i> (HF)	-214.643467	-217.930365	-217.935453	-217.939305	-217.940855	-217.940855
<i>E</i> (MP2)	-214.927356	-218.312214	-218.397281	-218.401965	-218.401965	-218.425804
ΔE^{MP2}	-5.35	-3.94	-4.17	-4.21	-4.22	-4.22
BSSE	23.95	3.31	2.42	1.45	1.44	1.44
BSSE ^b	2.64	2.67	1.45	1.15	1.25	1.25
BSSE ^c	21.31	0.64	0.97	0.30	0.19	0.19
	Basis set ^d					
	Ne 6s4p1d	8s4p1d	8s4p1d	6s4p3d	6s4p2d1f	6s4p2d1f
Ne	6s4p1d	8s4p1d	8s4p1d	6s4p1d	8s4p2d	6s4p2d1f
Be	6s4p1d	6s4p1d	8s4p1d	6s4p1d	8s4p2d	6s4p2d1f
O	6s4p1d	6s4p1d	8s4p1d	6s4p1d	8s4p2d	6s4p2d1f
<i>E</i> (HF)	-217.939146	-217.939387	-217.956373	-217.939310	-217.941205	-217.942384
<i>E</i> (MP2)	-218.365217	-218.365476	-218.399096	-218.424517	-218.427553	-218.448820
ΔE^{MP2}	-4.38	-4.38	-4.31	-4.38	-4.64	-4.76
BSSE	2.19	2.17	1.93	2.09	2.21	2.31
BSSE ^b	1.98	1.97	1.77	1.82	1.95	2.15
BSSE ^c	0.21	0.20	0.16	0.27	0.26	0.16

^a Ne-Be 17.58 pm, Be-O 13.47 pm, taken from refs^{1,2}; ^b deepening of the energy of Ne by the "ghost" orbitals of BeO; ^c deepening of the energy of BeO by the "ghost" orbitals of Ne; ^d Ne-Be 18.60 pm, Be-O 13.47 pm, MP2 optimization (corrected for the BSSE) with 6s4p1d, 6s4p1d, 6s4p1d basis set.

Reoptimization of the geometry with the $6s4p1d$, $6s4p1d$, $6s4p1d$ basis sets results in longer Ne-Be distances; the potential surface however is very flat. Such basis set extensions lead to slightly larger stabilization energies; however, the BSSE remains nearly constant. Its value is affected neither by extension of the occupied space nor by extension of the virtual space. At the HF level, the BSSE is smaller, and amounts only to 1 kcal/mol with the largest basis set. To reduce the BSSE further would require even larger basis sets, especially for neon.

ArBeO. Pilot calculations using $6s5p1d$, $6s4p1d$, $6s4p1d$ bases on Ar, Be, and O, respectively, showed the BSSE to be rather small. Using this basis set, we reoptimized the geometry keeping BeO rigid (Be—O 13.47 pm);^{1,2} the energy lowering (MP2, corrected for BSSE) was about 0.5 kcal/mol. The effects of larger basis sets were then studied using this new geometry. Results are summarized in Table IV. Extension of the polarization space on Ar increases the association energy and decreases in BSSE as well; further extension, from $2d$ to $3d$, is connected with minor changes only. Addition of f -functions on all the atoms results in small increases both in association energy and in BSSE. This is understandable, because the f -functions are diffuse. Further reduction of BSSE would require, as with NeBeO, extension of the noble gas basis set.

DISCUSSION

Tables II–IV show that the association energy of HeBeO has almost converged at the levels we have employed, but this is less so for NeBeO and ArBeO. Larger basis sets should increase the association energies somewhat. Nevertheless, we may conclude that HeBeO and NeBeO possess very similar association energies, but that of ArBeO is at least twice as large. What is the reason for comparable stability of HeBeO and NeBeO? The noble gases are expected to transfer electrons to BeO. A simple prediction based on the frontier orbital energies would give the following stability order: ArBeO \gg NeBeO $>$ HeBeO. However, the surprisingly low LUMO energy of He facilitates reverse electron transfer from BeO towards He. Such transfer is less probable with ArBeO and especially so with NeBeO. Those simple predictions are confirmed by natural atomic orbital and natural bond orbital analysis^{14,15} (cf. Table V). The total charge transfer energy, evaluated with the second-order perturbation theory from the natural bond orbital Fock matrix, is largest with ArBeO, while that of NeBeO is smaller than that of HeBeO. There are two reasons for smaller charge transfer energy of NeBeO in comparison with HeBeO: first, $\Delta E_{CT} \text{ He} \rightarrow \text{BeO}$ is larger than $\Delta E_{CT} \text{ Ne} \rightarrow \text{BeO}$; second, the reverse charge transfer with HeBeO is larger than with NeBeO. The larger value of reverse charge transfer for HeBeO is understandable. But why is the charge transfer between He and BeO larger than between Ne and BeO? The HOMO and LUMO energies of electron donor and electron acceptor lead to the opposite expectation. The explanation is

TABLE IV
 HF and MP2 energies, MP2 stabilization energies (ΔE^{MP2}) and basis set superposition errors (BSSE) for ArBeO. Geometry taken from MP2 optimization (corrected for the BSSE) with $6s5p1d$, $6s4p1d$, $6s4p1d$ basis set: Ar-Be 21.56 pm, Be-O 13.47 pm; energies in a. u. and kcal/mol, 1 a. u. = 2 625.5 kJ/mol, 1 kcal/mol = 4.184 kJ/mol

Quantity	Basis set					
	Ar $6s5p1d$ Be $6s4p1d$ O $6s4p1d$	$6s5p2d$ $6s4p1d$ $6s4p1d$	$6s5p3d$ $6s4p1d$ $6s4p1d$	$6s5p2d$ $6s4p2d$ $6s4p2d$	$6s5p2d1f$ $6s4p2d1f$ $6s4p2d1f$	
$E(\text{HF})$	-616.225197	-616.226029	-616.226285	-616.227573	-616.229378	
$E(\text{MP2})$	-616.575684	-616.633963	-616.655466	-616.658217	-616.690384	
ΔE^{MP2}	-8.38	-9.38	-9.47	-9.54	-10.12	
BSSE	2.03	1.34	1.39	1.43	2.02	
BSSE ^a	1.80	1.08	0.97	1.22	1.87	
BSSE ^b	0.23	0.26	0.32	0.21	0.15	

^a Deepening of the energy of Ar by the "ghost" orbitals of BeO; ^b deepening of the energy of BeO by the "ghost" orbitals of Ar.

simple: the charge transfer energy depends not only on the energy difference between HOMO of donor and LUMO of acceptor but also on the overlap of these orbitals. Data in Table V make evident that this overlap is larger with HeBeO than with NeBeO.

ΔE_{CT} is considerably larger with HeBeO than with NeBeO; however, the association energies of both complexes are comparable. This is due to another factor. Because of the greater polarizability of neon, the induction energy for NeBeO should be considerably larger than the induction energy of HeBeO. The total attraction energy, comprised mainly of charge transfer and of induction energy, is comparable for both molecules.

Electron transfer from the noble gases to BeO is proportional to the association energy with all three complexes. This indicates a predominately covalent rather than a van der Waals description of these molecules which also is supported by the minor effects of electron correlation. Note the small magnitude of the changes in dissociation energies determined at HF and post HF levels: HeBeO 4.49 vs 4.80; NeBeO 4.53 vs 4.76; ArBeO 9.56 vs 10.12 kcal/mol.

CONCLUSION

The HeBeO, NeBeO, and ArBeO complexes were investigated using extended basis sets at the MP2 level. While the basis set superposition error with all these molecules are small, it should still be corrected for. The stabilization energies of HeBeO and NeBeO are comparable, while that of ArBeO is considerably larger. The similar stabilization of HeBeO and NeBeO, not expected from qualitative MO theory, is

TABLE V

Natural bond orbital analysis of HeBeO, NeBeO and ArBeO evaluated with the largest basis sets at optimal geometry (see Tables I, II, and III); energies in kcal/mol, 1 kcal/mol = 4.184 kJ/mol

Molecule	$-\Delta E^a$	$-\Delta E_{CT}^b$	$-\Delta E_{CT}^c$	$-\Delta E_{CT}^d$	$q(X)^e$	$q(Be)^f$	$q(O)$	Δq^g	S^h
HeBeO	4.80	27.68	23.99	3.69	0.028	1.659	-1.687	0.028	0.416
NeBeO	4.76	19.78	18.90	0.88	0.024	1.677	-1.701	0.024	0.326
ArBeO	10.12	37.04	35.70	1.34	0.058	1.643	-1.700	0.058	0.483

^a MP2 stabilization energy; ^b charge-transfer energy determined by the second-order perturbation theory from the natural bond orbital Fock matrix; ^c charge-transfer energy (X → BeO); ^d charge-transfer energy (BeO → X); ^e X = He, Ne, Ar, resp.; ^f $q(Be)$ in isolated BeO is 1.700; ^g charge transferred from noble gas to the BeO; ^h overlap between the hybrids AO of electron donor (noble gas) and electron acceptor (BeO).

explained by larger energy gain due to charge transfer in HeBeO. This is caused (i) by the more favourable overlap between the occupied He orbital and the unoccupied orbitals of BeO, and (ii) by the existence of reverse charge transfer (from BeO to He).

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