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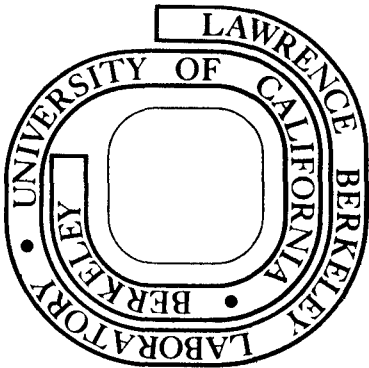
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Tetrahedral Be₄*

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Small metal clusters are of particular interest for at least two reasons: a) the crucial role they appear to play in catalytic processes,¹⁻⁵ and b) their existence as important species in the high temperature chemistry of metal vapors.⁶⁻⁸ Primarily as a result of the current surge of interest⁹ in surface chemistry, there have been a number of recent theoretical studies of small metal clusters.¹⁰⁻²²

In our own research, beryllium metal clusters as large as Be_{22} have been studied.²³ There we found the intriguing result that tetrahedral Be_4 appears to be the smallest significantly bound Be metal cluster. Be_2 , of course, is only weakly bound,²⁴ with a dissociation energy in all likelihood less than that of Mg_2 (for which $D_0 = 1.2 \text{ kcal/mole}$ ²⁵). Further Be_3 does not appear to be appreciably bound. Hence the goal of the present note is to examine at a higher level of theory the structure and energetics of Be_4 .

Our earlier reported²³ single-configuration self-consistent-field results for Be_4 are summarized on the first two lines of Table I. As noted in reference 16 of our earlier paper, these Be_4 clusters were not perfectly tetrahedral, since the three surface bonds are of length 2.2866 Å, while the three bonds to the second layer atom are 2.2855 Å. However in the new calculations reported here, perfect tetrahedral symmetry was assumed, and for each basis set the bond distance was optimized.

We now proceed to a discussion of the new Be_4 results. Basis set 1 (line 3 of Table I) was the Pople STO-3G minimum basis set,²⁶ but with orbital exponents optimum for Be_4 . The optimum exponents have values

$\zeta(1s) = 3.687$, $\zeta(2s) = \zeta(2p) = 1.003$, compared with the Be atom values $\zeta(1s) = 3.685$, $\zeta(2s) = 0.956$. As Table I shows, the optimization of basis set and geometry increase the predicted minimum basis dissociation energy from 16.2 to 30.0 kcal/mole. Similarly, geometry optimization using the previously described²³ double zeta (9s 2p/4s 2p) basis increases D_e from 19.4 to 21.2 kcal/mole.

Next a set of six d-like functions (orbital exponent $\alpha = 0.6$) was added to each Be atom. This basis yielded the results seen on the fifth line of Table I. Specifically, the predicted bond distance was decreased by 0.028 Å and the dissociation energy increased by 11.1 kcal/mole. Thus we see that d functions (polarization functions) appear to have a particularly large effect ($\sim 50\%$) on the predicted dissociation energy.

Calculations 2-6 in Table I employ the same (9s) primitive gaussian basis²⁷ used previously. However, a larger (4p) primitive set, optimized²⁸ for the 3P state of the Be atom, was used in the final three sets of calculations. Calculation 4 uses this new (9s 4p) basis in a standard double zeta contraction. There we see that the new (4p/2p) basis represents a significant improvement over the earlier (2p/2p) set. For this reason, d functions were also added to this second double zeta basis and the ensuing results are summarized as calculation number 5. Comparison of 4 and 5 shows that d functions contribute only 4 kcal/mole to the dissociation energy when an adequate set of Be p functions is adopted.

Finally, in calculation 6, the (4s 2p) contraction of the (9s 4p) primitive set was relaxed to (5s 3p). Comparison of calculations 4 and

6 shows that this increased flexibility actually decreases the predicted D_e slightly, since the energy improvement for four separated Be atoms is greater than the corresponding improvement for Be_4 . Thus we conclude that the Hartree-Fock dissociation energy of Be_4 is probably quite close to 40 kcal/mole. In general, of course, one expects²⁹ the correlation energy of molecular species to be significantly greater than that of the separated atoms. For Be_4 , however, this tendency may be diminished since the molecule makes heavy use of p functions, while p functions are excluded by symmetry considerations from the single-configuration wave functions for the isolated Be atoms. Hence the Hartree-Fock dissociation energy may be fairly close to the true value of D_e .

Finally, in Table II are given orbital energies and Mulliken populations for the most extensive wave function reported for Be_4 . There it is seen, as for several larger Be_n clusters,²² that the valence shell hybridization is roughly sp.

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TABLE I. Summary of theoretical predictions of the structure and dissociation energy of Be_4 .

Gaussian Basis Set	Total Energy (hartrees)	Bond Distance (Å)	Dissociation Energy D_e (kcal/mole)
Be(6s 3p/2s 1p)	-57.5934	a	16.2
Be(9s 2p/4s 2p)	-58.3125	a	19.4
1. Be(6s 3p/2s 1p)	-57.6154	2.121	30.0
2. Be(9s 2p/4s 2p)	-58.3154	2.155	21.2
3. Be(9s 2p 1d/4s 2p 1d)	-58.3330	2.127	32.3
4. Be(9s 4p/4s 2p)	-58.3391	2.095	36.1
5. Be(9s 4p 1d/4s 2p 1d)	-58.3455	2.085	40.1
6. Be(9s 4p/5s 3p)	-58.3414	2.085	35.8

^a Geometry not optimized, but rather assumed to be that of Be metal: $a_0 = 2.2866 \text{ \AA}$, $c_0 = 3.5833 \text{ \AA}$; see J. Donohue, The Structure of the Elements (Wiley, New York, 1974).

TABLE II. Orbital energies and Mulliken populations for tetrahedral Be_4 at its equilibrium geometry ($r = 2.0846 \text{ \AA}$). The (9s 4p 1d/4s 2p 1d) basis set described in the text was used.

Orbital	ϵ	Mulliken populations		
		Be s	Be p	Be d
$1a_1$	-4.69750	1.996	0.000	0.004
$1t_2$	-4.69668	5.988	0.000	0.012
$2a_1$	-0.55068	1.581	0.373	0.046
$2t_2$	-0.27247	2.872	3.070	0.057
Totals per unit		3.109	0.861	0.030

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