JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

COMMUNICATION

pubs.acs.org/JACS

Planar Tetracoordinate Carbon versus Planar Tetracoordinate Boron: The Case of CB_4 and Its Cation

Zhong-hua Cui,[†] Maryel Contreras,[‡] Yi-hong Ding,[*,†] and Gabriel Merino[*,‡]

[†]State Key Laboratory of Theoretical and Computational Chemistry, Institute of Theoretical Chemistry, Jilin University, Changchun 130023, People's Republic of China

[‡]Departamento de Química, Universidad de Guanajuato, Noria Alta s/n, 36050 Guanajuato, Mexico

Ⓢ *Supporting Information*

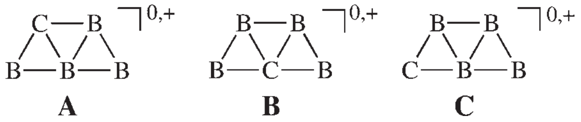
ABSTRACT: In this study, we analyzed CB_4 and its cation, CB_4^+. Using CCSD(T)/aug-cc-pVQZ//CCSD(T)/aug-cc-pVTZ quantum-chemical calculations, we found that the neutral molecule is in accord with the results of Boldyrev and Wang, having a C_s global minimum with a planar tricoordinate carbon structure, contradicting previous studies. In contrast, CB_4^+, which was reported by an early mass spectroscopic study, has a planar tetracoordinate carbon (ptC) atom, demonstrating that a modification of the charge can promote the stabilization of a ptC structure.

Forty years ago, Hoffmann, Alder, and Wilcox established some fundamental bases for stabilization of the planar tetracoordinate carbon (ptC) structure.[1] These rules have generated widespread interest in the chemical community and motivated an extensive experimental and theoretical search exploring possible ptC compounds.[2−13]

One of the strategies suggested for stabilizing a ptC is based on the replacement of the hydrogens in planar methane by substituents that are (i) σ donors, to facilitate electron transfer to the electron-deficient carbon, and (ii) π acceptors, to delocalize the p- or π-type lone pair.[7] Thus, boron seems to be a good option for stabilizing a ptC atom.[14−31] Actually, several planar hypercoordinate carbon structures using boron as ligands have been proposed in silico.[32,33] In 2000, Exner and Schleyer suggested that CB_6^{2-} could adopt a structure containing a planar hexacoordinate carbon atom.[34] This divining structure immediately caught the attention of the chemical community. In 2008, Averkiev and co-workers showed that the D_{6h} form is not the global-minimum structure.[35] A similar situation was found for CB_7^-,[36] CB_8, and CB_8^-.[25] The higher electronegativity of carbon relative to boron clearly disfavors the hypercoordinate carbon arrangements.[37,38]

Surprisingly, the simplest neutral pentaatomic boron−carbon cluster, CB_4, seems to be a strange case. In 2008, Pei and Zeng carried out a computational study on a set of carbon−boron mixed clusters at the CCSD(T)/cc-pVTZ//MP2/cc-pVTZ level.[39] In contrast to previous density functional theory calculations reported by Liu et al.[40] and Sateesh et al.,[21] Pei and Zeng claimed that the singlet ptC structure corresponded to the CB_4 global minimum and that the second most stable form, which contains a dicoordinate carbon, is less stable than the ptC structure by 1.67 kcal/mol. Nevertheless, Pei and Zeng noted a strong variation in the energy difference when the level of theory was changed.[39] Can a higher-level treatment again vary this trend?

Scheme 1



The choice for the treatment of electron correlation, when computationally is feasible, is the coupled cluster method including single, double, and perturbatively connected triple excitations [CCSD(T)].[41] Its accuracy has been well-established for chemical problems that are not severely multireference in nature.

In this work, CCSD(T)/aug-cc-pVQZ//CCSD(T)/aug-cc-pVTZ computations including zero-point energy (ZPE) corrections were employed in the pursuit of accurate structures and relative energies for the lowest-energy forms of CB_4. Using this sophisticated level, we found that the most stable form contains a planar tetracoordinate boron (ptB) atom, in agreement with the results of Boldyrev and Wang.[25,35] The question that naturally arises is whether there exists a way to stabilize a ptC using boron atoms as ligands. Hoping that altering the molecular charge might encourage stabilization of a ptC, we explored the potential energy surface (PES) of CB_4^+. Gratifyingly, we found that the most stable form of this experimentally detected cation has a ptC.

In order to explore systematically the PES of the title complex, the GXYZ stochastic search[42] and grid-based comprehensive isomeric search[43] strategies were performed at the B3LYP/6-31G(d) level to generate the starting points, which were further optimized at the B3LYP/6-311+G(d) level. The six low-lying structures were reoptimized at the MP2/aug-cc-pVTZ and CCSD(T)/aug-cc-pVTZ levels. Every stationary point on the PES was characterized by a harmonic analysis using the same theoretical methodology that was employed in the geometry optimization. Minima connected by a given transition state were confirmed by intrinsic reaction coordinate (IRC) calculations. Single-point calculations for the three lowest-energy isomers were done at the CCSD(T)/aug-cc-pVQZ//CCSD(T)/aug-cc-pVTZ level, as were complete basis set (CBS) extrapolation calculations [i.e., CCSD(T)_CBS].[44] The above calculations were carried out using Gaussian 03.[45]

Received: April 21, 2011
Published: July 28, 2011

Table 1. Relative Energies of CB_4 and CB_4^+ Isomers[a]

	^{1}**A**	^{3}**A**	^{1}**B**	^{3}**B**	^{1}**C**	^{3}**C**	^{2}**A**$^+$	^{2}**B**$^+$	^{2}**C**$^+$
symmetry	C_s	C_1	C_{2v}	C_2	C_s	C_s	C_s	C_{2v}	C_s
B3LYP/aug-cc-pVTZ	0.0	−6.2	2.6	−0.7	−4.1	−7.3	0.0	0.1	6.0
MP2/aug-cc-pVTZ	0.0	0.1	−4.9	2.6	0.0	13.1	0.0	−0.3	–
CCSD(T)/aug-cc-pVTZ//B3LYP/aug-cc-pVTZ	0.0	5.0	1.0	10.1	2.6	3.7	0.0	−0.3	5.5
CCSD(T)/aug-cc-pVTZ//MP2/aug-cc-pVTZ	0.0	8.8	1.8	11.5	2.2	4.5	0.0	−0.7	–
CCSD(T)/aug-cc-pVTZ	0.0	5.5	1.3	10.6	2.6	4.2	0.0	−0.3	–
CCSD(T)/aug-cc-pVQZ//CCSD(T)/aug-cc-pVTZ	0.0	5.5	1.4	10.6	2.7	4.2	0.0	−0.3	–
CCSD(T)_CBS	0.0	5.6	1.4	10.7	2.8	4.2	0.0	−0.2	–

[a] All values are in kcal/mol. Each energy includes ZPE corrections.

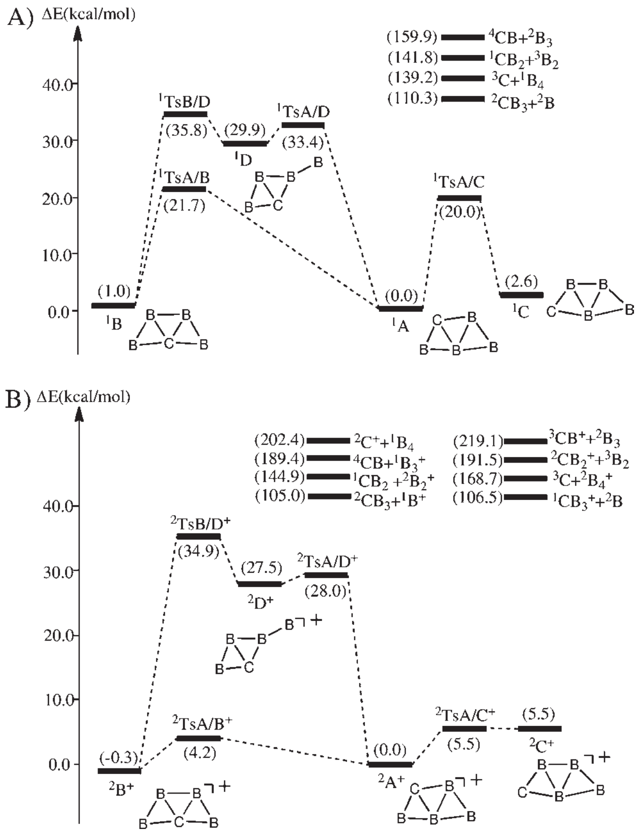


Figure 1. Potential energy surfaces for the three kinds of low-lying isomers of (A) CB_4 and (B) CB_4^+. The energy differences were obtained at the CCSD(T)/aug-cc-pVTZ//B3LYP/aug-cc-pVTZ+ZPVE level. The energy values are in kcal/mol.

The initial exploration of both the singlet and triplet surfaces at the B3LYP/6-311+G(d) level eventually produced a total of 16 singlet and 13 triplet local minima. The structures of the three lowest-energy singlet isomers together with the corresponding triplet ones are illustrated in Scheme 1. Complete optimized geometries are available in the Supporting Information (SI). The B3LYP and MP2 relative energies of the six conformations (three singlets and three triplets) of interest are given in Table 1. The notation ^{1}**A** refers to the singlet neutral structure **A**, and ^{2}**B**$^+$ refers to the doublet cation structure **B**. This nomenclature will be used in the subsequent discussion.

The lowest-energy conformation is predicted to be the triplet planar dicoordinate carbon structure ^{3}**C** by B3LYP and the singlet planar tetracoordinate carbon structure ^{1}**B** by MP2. The lack of consistency in Table 1 is problematic, and even worse, the results are the opposite of those computed by Pei and Zeng.[39]

To obtain more reliable relative energies, single-point energies at the CCSD(T)/aug-cc-pVTZ//B3LYP/aug-cc-pVTZ level were obtained (Table 1). Interestingly, ^{1}**B**, the isomer suggested by Pei and Zeng as the global minimum, lies above the singlet planar tricoordinate carbon form ^{1}**A** by ∼1 kcal/mol.[39] The next highest arrangement is ^{1}**C**, which is 2.6 kcal/mol less stable than ^{1}**A**. The same trend was obtained at the CCSD(T)/aug-cc-pVTZ//MP2/aug-cc-pVTZ level.

On the basis of these results and in order to avoid any source of error, the most stable structures were reoptimized at the CCSD(T)/aug-cc-pVTZ level, and the relative energies were then computed at the CCSD(T)/aug-cc-pVQZ//CCSD(T)/aug-cc-pVTZ level followed by the energy extrapolation to the complete basis set (CBS) limit. In all cases, the tendency was similar to that obtained using the geometries computed at the B3LYP and MP2 levels. The CCSD(T) energies reported here are consistent with the results of Boldyrev and Wang, who observed that carbon avoids planar hypercoordination.[25,35] Thus, the most stable structure of CB_4 has a ptB atom.

Figure 1A summarizes the interconversion pathways of CB_4. It is apparent that the lowest-energy isomerization pathway between the three lowest-energy singlet isomers (^{1}**A**, ^{1}**B**, and ^{1}**C**) is associated with a "bond-stretch" mechanism. Notably, the lowest isomerization barriers are >20 kcal/mol. These activation energies are enough to ensure a half-life of 1 day. The direct conversion between ^{1}**B** and ^{1}**C** would be associated with an unlikely process wherein the carbon coordination number changes from 4 to 2. Indeed, we did not find the transition state related to this transformation. In addition, an alternative pathway between ^{1}**A** and ^{1}**B** was located via a high-energy intermediate ^{1}**D**, whose energy is higher than that of ^{1}**A** by 29.9 kcal/mol. Finally, several CB_4 fragmentation pathways were computed, namely, ^{3}C + $^1B_4$ (139.2), ^{4}CB + $^2B_3$ (159.9), $^1CB_2$ + $^3B_2$ (141.8), and $^2CB_3$ + ^{2}B (110.3) (Figure 1A, upper right); these results show that CB_4 is resistant to fragmentation.

Various carbon–boron binary species have been generated via the vaporization of boron/carbon powders and characterized by FTIR spectroscopy in low-temperature argon matrixes (e.g., CB_2,[46] BC_2,[47] and C_2B_2 and C_3B[48]). We strongly hope that CB_4 with three distinct isomers could be detectable under similar conditions. The calculated IR spectra of ^{1}**A**, ^{1}**B**, and ^{1}**C** obtained using various high levels of theory are collected in the SI.

The above results contrast with our initial expectation: boron atoms can act as stabilizing ligands to achieve a global ptC.

Clearly, structure ^{1}**B** is close in energy to the lowest-energy structure ^{1}**A**. Hoping to find a ptC, we decided to explore the PESs of the charged forms CB_4^- and CB_4^+. Pei and Zeng analyzed the CB_4^- PES at the CCSD(T)/6-311+G(d,p) level and found that the ptC structure is higher in energy than the most stable one by 23.6 kcal/mol.[39] Surprisingly, CB_4^+ had not received any theoretical attention to date. We therefore carried out a careful structural search looking for the CB_4^+ cation in both doublet and quartet states at the B3LYP/6-311+G(d) level.

For CB_4^+, the quartet states are less stable than the doublet ones by more than 30 kcal/mol. Figure 1B depicts the isomers found within 15 kcal/mol above the global minimum computed at the CCSD(T)/aug-cc-pVTZ//B3LYP/aug-cc-pVTZ level. Interestingly, ^{2}**A**$^+$ and ^{2}**B**$^+$ are almost isoenergetic (the energy difference is just 0.3 kcal/mol). This relative energy computed at the CCSD(T)/aug-cc-pVQZ//CCSD(T)/aug-cc-pVTZ level is the same. Moreover, we noticed that the Hartree−Fock wave function spin-contamination value ($\langle S^2\rangle$) of ^{2}**A**$^+$ and ^{2}**B**$^+$ was ~1.4 in our CCSD(T) methods. It is generally considered that coupled-cluster calculations are much less influenced by spin contamination than Möller−Plesset ones. To confirm our coupled-cluster results, we carried out CASSCF(13,14)/(CASPT2) calculations [i.e., geometry optimization at the complete active space self-consistent field (CASSCF) level[49] with 13 active electrons and 14 active orbitals and energy evaluation at the complete active space second-order perturbation theory (CASPT2) level[50]] using MOLCAS-7.[51,52] With the aug-cc-pVTZ basis set and a large ANO-RCC[53] (atomic natural orbital−relativistic with core correlation, i.e., contraction of 8s7p4d3f and 9s9p5d3f for C and B atom, respectively) basis set, our CASSCF(13,14)/CASPT2 calculations showed that ^{2}**B**$^+$ is more stable than ^{2}**A**$^+$ by 0.6 and 0.2 kcal/mol, respectively, confirming the CCSD(T) results. Kinetically, the “bond-stretch” transition states leading to ^{2}**B**$^+$ and ^{2}**C**$^+$ lie 4.2 and 5.5 kcal/mol above ^{2}**A**$^+$, respectively. By scrutinizing the structural properties, we found that the inner C−B or B−B bonds of CB_4^+ are somewhat elongated with respect to those in neutral CB_4 (see the SI). The slightly longer inner C−B and B−B distances result in the easy “bond-stretch” process for ^{2}**A**$^+$, ^{2}**B**$^+$, and ^{2}**C**$^+$. In the ptC structure at the CCSD(T)/aug-cc-pVTZ level, for example, the C_{2v}-symmetric CB_4^+ has an inner C−B bond length of 1.783 Å, while that in neutral CB_4 is 1.646 Å. The outer C−B distance is a changed by a small amount, from 1.468 Å in CB_4^+ to 1.511 Å in CB_4. Clearly, the PES is smoother in CB_4^+ than in CB_4 (Figure 1B).

The interesting result is that ^{2}**B**$^+$ contains a ptC! Remarkably, this species was detected via laser mass spectrometry of boron carbide by Becker and Dietze in 1988.[54] The present quantum-chemical studies show for the very first time that the ground state of CB_4^+ has a ptC structure, although the tricoordinate carbon structure is quite competitive and might also coexist.

Thus, in this work we have shown that a previously unrecognized singlet isomer with a planar tricoordinate carbon, ^{1}**A**, is the global minimum for CB_4, in contrast to the structure recently predicted by Pei and Zeng. Clearly, this indicated that carbon avoids the central position in CB_4, in agreement with the Boldyrev−Wang results. Surprisingly, we found that a modification of the molecular charge could induce the formation of a ptC species. The lowest-energy isomer of CB_4^+ contains a ptC, and more interestingly, such a species was reported in an early mass spectroscopic study.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Complete ref 45; structures and energies of the isomers and transition states of CB_4 and CB_4^+; and calculated IR spectra of ^{1}**A**, ^{1}**B**, and ^{1}**C** of CB_4. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

yhdd@jlu.edu.cn; gmerino@quijote.ugto.mx

■ ACKNOWLEDGMENT

This work was supported by the National Key Basic Research and Development Program of China (2010CB327701), the National Natural Science Foundation of China (20773054, 60977024, 21073074), the Doctor Foundation of the Ministry of Education (20070183028), the Excellent Young Teacher Foundation of the Ministry of Education of China, the Excellent Young People Foundation of Jilin Province (20050103), and the Program for New Century Excellent Talents in University (NCET). The work in Mexico was supported by CONACYT (Grant 57892). M.C. acknowledges the Ph.D. fellowship from CONACYT. We thank the referees for many illuminating comments.

■ REFERENCES

(1) Hoffmann, R.; Alder, R. W.; Wilcox, C. F., Jr. *J. Am. Chem. Soc.* **1970**, *92*, 4992.
(2) Sorger, K.; Schleyer, P. v. R. *THEOCHEM* **1995**, *338*, 317.
(3) Radom, L.; Rasmussen, D. R. *Pure Appl. Chem.* **1998**, *70*, 1977.
(4) Siebert, W.; Gunale, A. *Chem. Soc. Rev.* **1999**, *28*, 367.
(5) Keese, R. *Chem. Rev.* **2006**, *106*, 4787.
(6) Merino, G.; Mendez-Rojas, M. A.; Vela, A.; Heine, T. *J. Comput. Chem.* **2007**, *28*, 362.
(7) Collins, J. B.; Dill, J. D.; Jemmis, E. D.; Apeloig, Y.; Schleyer, P. v. R.; Seeger, R.; Pople, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 5419.
(8) Schleyer, P. v. R.; Boldyrev, A. I. *Chem. Commun.* **1991**, 1536.
(9) Li, X.; Wang, L. S.; Boldyrev, A. I.; Simons, J. *J. Am. Chem. Soc.* **1999**, *121*, 6033.
(10) Boldyrev, A. I.; Simons, J. *J. Am. Chem. Soc.* **1998**, *120*, 7967.
(11) Li, X.; Zhang, H. F.; Wang, L. S.; Geske, G. D.; Boldyrev, A. I. *Angew. Chem., Int. Ed.* **2000**, *39*, 3630.
(12) Boldyrev, A. I.; Li, X.; Wang, L. S. *J. Chem. Phys.* **1999**, *111*, 4993.
(13) Wang, L. S.; Boldyrev, A. I.; Li, X.; Simons, J. *J. Am. Chem. Soc.* **2000**, *122*, 7681.
(14) Gribanova, T. N.; Minyaev, R. M.; Minkin, V. I. *Collect. Czech. Chem. Commun.* **1999**, *64*, 1780.
(15) Minyaev, R. M.; Gribanova, T. N.; Starikov, A. G.; Minkin, V. I. *Dokl. Chem.* **2002**, *382*, 41.
(16) Erhardt, S.; Frenking, G.; Chen, Z. F.; Schleyer, P. v. R. *Angew. Chem., Int. Ed.* **2005**, *44*, 1078.
(17) Minyaev, R. M.; Gribanova, T. N.; Minkin, V. I.; Starikov, A. G.; Hoffmann, R. *J. Org. Chem.* **2005**, *70*, 6693.
(18) Park, S. S. *Bull. Korean Chem. Soc.* **2005**, *26*, 63.
(19) Wu, Y. B.; Yuan, C. X.; Yang, P. *THEOCHEM* **2006**, *765*, 35.
(20) Ito, K.; Chen, Z. F.; Corminboeuf, C.; Wannere, C. S.; Zhang, X. H.; Li, Q. S.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **2007**, *129*, 1510.
(21) Sateesh, B.; Reddy, A. S.; Sastry, G. N. *J. Comput. Chem.* **2007**, *28*, 335.
(22) Shahbazian, S.; Alizadeh, S. *J. Phys. Chem. A* **2008**, *112*, 10365.
(23) Sun, W. X.; Zhang, C. J.; Cao, Z. X. *J. Phys. Chem. C* **2008**, *112*, 351.

(24) Zhang, C. J.; Sun, W. X.; Cao, Z. X. *J. Am. Chem. Soc.* **2008**, *130*, 5638.

(25) Averkiev, B. B.; Wang, L. M.; Huang, W.; Wang, L. S.; Boldyrev, A. I. *Phys. Chem. Chem. Phys.* **2009**, *11*, 9840.

(26) Liang, J. X.; Jia, W. H.; Zhang, C. J.; Cao, Z. X. *Acta Phys.-Chim. Sin.* **2009**, *25*, 1847.

(27) Wu, X. J.; Pei, Y.; Zeng, X. C. *Nano Lett.* **2009**, *9*, 1577.

(28) Liang, J. X.; Zhang, C. J. *Acta Chim. Sin.* **2010**, *68*, 7.

(29) Shao, C. B.; Ding, Y. H. *Phys. Chem. Chem. Phys.* **2010**, *12*, 13153.

(30) Zhang, C. J.; Jia, W. H.; Cao, Z. X. *J. Phys. Chem. A* **2010**, *114*, 7960.

(31) Xiao, B.; Ding, Y. H.; Sun, C. C. *Phys. Chem. Chem. Phys.* **2011**, *13*, 2732.

(32) Wang, Z. X.; Schleyer, P. v. R. *Science* **2001**, *292*, 2465.

(33) Islas, R.; Heine, T.; Ito, K.; Schleyer, P. v. R.; Merino, G. *J. Am. Chem. Soc.* **2007**, *129*, 14767.

(34) Exner, K.; Schleyer, P. v. R. *Science* **2000**, *290*, 1937.

(35) Averkiev, B. B.; Zubarev, D. Y.; Wang, L. M.; Huang, W.; Wang, L. S.; Boldyrev, A. I. *J. Am. Chem. Soc.* **2008**, *130*, 9248.

(36) Wang, L. M.; Huang, W.; Averkiev, B. B.; Boldyrev, A. I.; Wang, L.-S. *Angew. Chem., Int. Ed.* **2007**, *46*, 4550.

(37) Wang, L. M.; Averkiev, B. B.; Ramilowski, J. A.; Huang, W.; Wang, L. S.; Boldyrev, A. I. *J. Am. Chem. Soc.* **2010**, *132*, 14104.

(38) Galeey, T. R.; Ivanov, A. S.; Romanescu, C.; Li, W. L.; Bozhenko, K. V.; Wang, L. S.; Boldyrev, A. I. *Phys. Chem. Chem. Phys.* **2011**, *13*, 8805.

(39) Pei, Y.; Zeng, X. C. *J. Am. Chem. Soc.* **2008**, *130*, 2580.

(40) Liu, C. H.; Tang, M. S.; Wang, H. M. *J. Phys. Chem. A* **2007**, *111*, 704.

(41) Pople, J. A.; Head-Gordon, M.; Raghavachari, K. *J. Chem. Phys.* **1987**, *87*, 5968.

(42) Lu, H. G.; Wu, Y. B. *GXYZ: A Random Cartesian Coordinates Generating Program*; Shanxi University: Taiyuan, China, 2008.

(43) Shao, C. B.; Ding, Y. H. *Grid-Based Comprenhensive Isomeric Search Algorithm*; Jilin University: Changchun, China, 2010.

(44) Halkier, A.; Helgaker, T.; Jorgensen, P.; Klopper, W.; Koch, H.; Olsen, J.; Wilson, A. K. *Chem. Phys. Lett.* **1998**, *286*, 243.

(45) Frisch, M. J.; et al. *Gaussian 03*, revision D.02; Gaussian, Inc.: Wallingford, CT, 2003.

(46) Larson, C. W.; Presilla-Marquez, J. D. *J. Chem. Phys.* **1996**, *105*, 3398.

(47) Presilla-Marquez, J. D.; Larson, C. W.; Carrick, P. G.; Rittby, C. M. L. *J. Chem. Phys.* **1996**, *105*, 3398.

(48) Presilla-Marquez, J. D.; Carrick, P. G.; Larson, C. W. *J. Chem. Phys.* **1999**, *110*, 5702.

(49) Roos, B. O. *Adv. Chem. Phys.* **1987**, *69*, 399.

(50) Andersson, K.; Malmqvist, P.-A.; Roos, B. O. *J. Chem. Phys.* **1992**, *96*, 1218.

(51) Aquilante, F.; De, V. L.; Ferre, N.; Ghigo, G.; Malmqvist, P.-A.; Neogrady, P.; Pedersen, T. B.; Pitonak, M.; Reiher, M.; Roos, B. O.; Serrano-Andres, L.; Urban, M.; Veryazov, V.; Lindh, R. *J. Comput. Chem.* **2010**, *31*, 224.

(52) Karlström, G.; Lindh, R.; Malmqvist, P.-A.; Roos, B. O.; Ryde, U.; Veryazov, V.; Widmark, P.-O.; Cossi, M.; Schimmelpfennig, B.; Neogrady, P.; Seijo, L. *Comput. Mater. Sci.* **2003**, *28*, 222.

(53) Roos, B. O.; Lindh, R.; Malmqvist, P.-A.; Veryazov, V.; Widmark, P. O. *J. Phys. Chem. A* **2004**, *108*, 2851.

(54) Becker, S.; Dietze, H. J. *Int. J. Mass Spectrom.* **1988**, *82*, 287.