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LETTERS

Density Functional Study of ^{59}Co Chemical Shielding Tensors Using Gauge-Including Atomic Orbitals

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We report the first successful density functional calculation of the ^{59}Co chemical shift span as well as the chemical shift skew of $[Co(NH_3)_6]Cl_3$ = (243 ppm, 0.57), $[Co(NH_3)_4CO_3]Br$ = (1562 ppm, 0.30), and Co(acac)$_3$ = (1115 ppm, −0.42) which agree satisfactorily with the experimental values; viz. $[Co(NH_3)_6]Cl_3$ = (308 ppm, 0.56), $[Co(NH_3)_4CO_3]Br$ = (1500 ppm, 0.33), and Co(acac)$_3$ = (1230 ppm, −0.51). We have conclusively demonstrated that hybrid HF-DFT XC functionals B3PW91 and B3LYP are more suitable for ^{59}Co shielding calculation compared to the pure density functional BLYP. Furthermore, the results of this study show that the performance of the B3PW91 functional is slightly superior to the B3LYP functional. It is suggested that B3PW91/6-311+G* or B3LYP/6-311+G* is promising for ^{59}Co shielding calculations.

Introduction

The accurate calculation of chemical shielding constants has been actively pursued because it can facilitate the use of NMR chemical shifts data in the study of electronic structures. Although the large chemical shifts range of transition metals provides a stringent test on the reliability of a computation method, relatively few ab initio shielding constants calculations are found for transition metals. In particular, Nakatsuji et al.[1] reported the first ab initio study of metal chemical shifts on several Cu, Zn, Ag, and Cd ($d^{10}s^{1-2}p^0$) complexes using the finite perturbations SCF method and a double-ζ plus p-polarization basis set. Together with the works on Ti, Nb, Mo, and Mn (d^n) complexes,[1] Nakatsuji has clarified the electronic origins and mechanisms of these transition-metal chemical shifts. In other laboratories, computational studies on Zn[2] and Mo[3] are also reported without considering electron correlation effects. Although it is widely accepted that the correlation effect should not be neglected in the shielding calculations of transition metals,[4] post-Hartree−Fock shielding calculation is not found for any transition metal.

The shielding constants of hexacoordinated Co(III) complexes, where the low-spin d^6 complexes have a closed $d(t_{2g})$ subshell with energetically low-lying $d(t_{2g}) \rightarrow d(e_g)$ transitions, is known to give rise to a large chemical shift range of ca. 12 000 ppm.[5] Significant electron-correlation effects are anticipated to dominate the paramagnetic terms of the ^{59}Co chemical shielding. Although the ab initio shielding calculations of other transition metals have been successful, relatively few calculations on ^{59}Co shielding constants are found in the literature.[6] Therefore, shielding calculation of ^{59}Co presents a serious challenge to the theoretical study of shielding constants and any progress in ^{59}Co shielding calculation may warrant a general progress for the shielding calculation of, at least, the first-row transition metals.

Recently, it has been demonstrated that molecular calculations may be performed by DFT methods with a quality comparable to that obtained from the post-Hartree−Fock methods.[7] Among the proposed DFT-NMR methods[8] for the calculation of shielding tensor, the uncoupled DFT-IGLO[8e] by Malkin et al. and the DFT-GIAO[8h,j] by Schreckenbach et al. and Rauhut et al. are equivalent in principle.[9] These three methods employ current-independent exchange correlation (XC) functionals and result in a substantial reduction of computational cost because

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it is no longer necessary to solve a set of coupled equations. If hybrid XC functionals (B3PW91 and B3LYP, empirical combination of HF exchange and density correlation functionals) are employed instead of pure density XC functionals (BLYP), the computational cost increases again because of the "reappearance" of the coupled equations. These hybrid XC functionals have been applied with success to the study of ^{13}C and ^{15}N shielding constants of molecules containing the first two row elements by Cheesman et al.[8k] Although the exact form of the current-dependent XC functional is not known, the work of Lee et al. represents the first implementation of the DFT shielding calculation which takes into account of the current dependent XC energy, viz. the CDFT-GIAO approach.[8i] Unfortunately, the calculated results are disappointing and the deficiency is ascribed to the inferior quality of the XC functional employed. On the other hand, Malkin et al. modify the energy terms in the sum over states approach by including an empirical term corresponding to the change in the exchange-correlation interaction of the excited states.[8f,g] The SOS-DFPT-IGLO method of Malkin et al. tends to provide good agreement with experiments for a number of organic and inorganic molecules containing atoms from both the first and second rows.[8g] The ^{51}V chemical shift tensors for a series of vanadate compounds (d^0) with a range of ca. 2000 ppm in isotropic shielding values are also satisfactorily reproduced.

These studies provide the stimulus for us to attempt DFT calculations intended to establish an economical and reliable method for the calculation of ^{59}Co shielding tensors. Coupled Hartree−Fock and DFT calculations are attempted in the present study. The performance of the SOS-DFPT-IGLO has been discussed elsewhere.[10] The calculated shielding tensors are compared with the experimental solid-state NMR data. The NATO convention for reporting the chemical shift tensor is used in this work.[11]

$$\delta_{ii} = \sigma_{ii}^{\text{ref}} - \sigma_{ii} \tag{1}$$

$$\delta_{\text{iso}} = {}^1/_3(\delta_{11} + \delta_{22} + \delta_{33}) \tag{2}$$

$$\delta_{11} \geq \delta_{22} \geq \delta_{33} \tag{3}$$

$$\text{span} \equiv \Omega = \delta_{11} - \delta_{33} \tag{4}$$

$$\text{skew} \equiv \kappa = \frac{2\delta_{22} - (\delta_{11} + \delta_{33})}{\Omega} \tag{5}$$

Computational Details

^{59}Co chemical shielding constants were calculated by HF-SCF and DFT methods using the Gaussian 94 package[12] running on a Unix workstation. The formalism of GIAO[13] is employed to treat the problem of gauge dependence. Among the many choices of the XC functionals available in Gaussian 94, B3LYP,[14] BLYP,[14b,15] and B3PW91[14a,16] were chosen for the DFT calculation of the ^{59}Co chemical shielding constants. While BLYP is considered as a pure density functional, B3LYP and B3PW91 are hybrid HF-DFT functional. A detail description of these XC functionals is referred to the Gaussian manual.[17] Standard Gaussian basis sets including 6-311G, 6-311+G*, 6-311++G*, 6-311+G(df), and 6-311++G(df) were used for the shielding calculation.

The coordinates of the atoms of *cis*-$[Co(en)_2(NO_2)_2]Cl$ were taken from the literature[18] where the C−H bond length was reproted to be ca. 1.00 Å. The coordinates of the hydrogen atoms which are missing in the reported structures[19,20] of $[Co(NH_3)_6]Cl_3$ and $[Co(NH_3)_4CO_3]Br$ were calculated by assuming a N−H bond legnth of 1.01 Å and a H−N−H bond angle of 106.7°. For the $Co(acac)_3$, the methyl groups of the ligands (CH_3−C) were replaced by H (H−C) with a bond length of 0.9 Å.[21] The structures of $K_3[Co(CN)_6]$ were taken from the work of Reynhardt.[22] All the calculations were performed on the bare complexes.

Results and Discussion

Calculations of $[Co(NH_3)_4CO_3]Br$. *Hartree−Fock.* As shown in Table 1, the agreement between the Hartree−Fock and the experimental results are poor although the diamagnetic shielding of ^{59}Co converges closely to the free atom value of 2166 ppm calculated by Malli.[23] This is not unexpected because the electron correlation effect is well-known to be of paramount importance in systems containing transition metals.[4] The poor trend of the Ω clearly demonstrates the incompatibility of the computational method. It is interesting to note that the calculated Ω varied insignificantly from 2486 to 2489 ppm when the basis set was changed from 6-311+G* to 6-311++G*. That is, the additional s-diffuse functions for hydrogen atoms does not play an important role in the ^{59}Co shielding calculation which is not surprising because ^{59}Co shielding constant is usually considered a local property. This observation is also found when correlation effect is taken into account (vide infra).

BLYP. The choice of BLYP, a pure DFT XC functional, results in an uncoupled DFT-GIAO shielding calculation. The calculated values of the ^{59}Co diamagnetic shielding term (σ^d) agree favorably with the HF values such that σ^d is shown to be insensitive to the correlation effect (same for other XC functionals). Although the BLYP functional has been shown to produce reliable results for the calculations of bond energies,[24] the performance of BLYP in ^{59}Co shielding calculation is far from satisfactory. The inferior quality of the BLYP functional in the calculations of vibrational circular dichroism and mid-IR absorption spectra has also been demonstrated recently.[25]

B3LYP. Calculations using the B3LYP functional confirm the importance of d-diffuse and f-polarization functions when the Ω and κ data obtained using the 6-311+G* and the 6-311G basis sets are compared. The satisfactorily reproduced Ω and κ data (calculated 1385 ppm and 0.28; experimental 1500 ppm and 0.33) clearly demonstrate the significance of the electron correlation effect in ^{59}Co shielding calculation. When a set of g-polarization function is added for the cobalt atom in 6-311++G(df), the calculated Ω and κ values (1367 ppm and 0.15) deviate further away from the experimental values. For the moment, we do not have an explanation but basis set imbalance may be a possible cause.[26] In a recent review, it has been pointed out that the polarization functions of different angular momenta must be kept in balance for a proper description of the valence space.[27]

B3PW91. The general trends obtained for the Ω and κ follow closely but slightly superior to that calculated by the B3LYP functional. Changing the basis set from 6-311++G* to 6-311+G(df) produces a better agreement between the experimental (1500 ppm) and calculated Ω (1549 ppm) but resulting in a poor agreement with κ (0.33 experimental; 0.18 calculated). Thus, it is shown that the g-polarization function is not necessary for ^{59}Co shielding calculation. Although the B3PW91 functional has not been studied extensively, this work demonstrates that the hybrid functional B3PW91 is a good option for shielding calculation.

Calculations of $[Co(NH_3)_6]Cl_3$. On the basis of the case study on $[Co(NH_3)_4CO_3]^+$, we suggest that the cost/efficiency ratio is optimal at B3PW91/6-311+G* or B3LYP/6-311+G* level for the calculation of ^{59}Co chemical shielding constants. A preliminary testing of this suggestion is carried out by

TABLE 1: Summary of the ^{59}Co Shielding Tensors Calculated for $[Co(NH_3)_4CO_3]Br$[a]

methods	σ^d (ppm)	σ^p (ppm)	σ_{iso} (ppm)	Ω (ppm), κ	$\Omega_{calc}/\Omega_{expt}$, $\kappa_{calc}/\kappa_{expt}$
HF					
6-311G	2140	−52425	−50284	1989, −0.23	1.32, −0.69
6-311+G*	2153	−47173	−45020	2486, 0.88	1.65, 2.66
6-311++G*	2160	−47298	−45038	2489, 0.90	1.66, 2.73
6-311++G(df)	2160	−47138	−44978	2845, 0.95	1.89, 2.88
BLYP					
6-311G	2146	−13170	−11024	755, 0.70	0.50, 2.12
6-311+G*	2153	−12271	−10118	999, 0.09	0.67, 0.27
6-311++G*	2156	−12277	−10121	996, 0.09	0.66, 0.27
6-311++G(df)	2156	−12278	−10123	988, −0.03	0.66, −0.09
B3LYP					
6-311G	2145	−16491	−14346	1061, 0.87	0.71, 2.64
6-311+G*	2153	−15528	−13375	1385, 0.28	0.92, 0.85
6-311++G*	2156	−15533	−13377	1379, 0.27	0.92, 0.82
6-311++G(df)	2156	−15535	−13379	1367, 0.15	0.91, 0.45
B3PW91					
6-311G	2144	−17122	−14977	1169, 0.86	0.78, 2.61
6-311+G*	2155	−16041	−13886	1562, 0.30	1.04, 0.91
6-311++G*	2159	−16046	−13887	1555, 0.29	1.04, 0.88
6-311+G(df)	2155	−16044	−13890	1549, 0.18	1.03, 0.55
experimental				1500, 0.33	

[a] The single-crystal NMR data are taken from ref 30.

TABLE 2: Summary of the ^{59}Co Shielding Tensors Calculated for $[Co(NH_3)_6]Cl_3$ at Two Crystallographically Nonequivalent Sites[a]

method	σ^d (ppm)	σ^p (ppm)	σ (ppm)	Ω (ppm), κ	$\Omega_{calc}/\Omega_{expt}$, $\kappa_{calc}/\kappa_{expt}$
			Site 2		
B3LYP					
6-311+G*	2151	−13904	−11753	63, 0.40	0.38, 0.61
6-311+G(df)	2150	−13899	−11748	65, 0.41	0.40, 0.62
6-311++G(df)	2154	−13893	−11739	64, 0.36	0.39, 0.55
B3PW91					
6-311+G*	2155	−14268	−12113	64, 0.34	0.39, 0.52
6-311+G(df)	2154	−14263	−12110	66, 0.36	0.40, 0.55
6-311++G(df)	2158	−14257	−12099	64, 0.30	0.39, 0.45
experimental				163, 0.66	
			Site 3		
B3LYP					
6-311+G*	2150	−13516	−11366	233, 0.59	0.76, 1.05
6-311+G(df)	2149	−13509	−11360	237, 0.60	0.77, 1.07
6-311++G(df)	2152	−13502	−11350	235, 0.60	0.76, 1.07
B3PW91					
6-311+G*	2153	−13849	−11696	243, 0.57	0.79, 1.02
6-311+G(df)	2152	−13844	−11692	248, 0.58	0.81, 1.04
6-311++G(df)	2156	−13836	−11680	245, 0.57	0.79, 1.02
experimental				308, 0.56	

[a] The single-crystal NMR data are taken from ref 31.

calculating the ^{59}Co shielding data of $[Co(NH_3)_6]^{3+}$ at two nonequivalent sites. The data are summarized in Table 2. The calculated Ω (243 and 233 ppm at B3PW91/6-311+G* and B3LYP/6-311+G* level, respectively) and κ (0.57 and 0.59 at B3PW91/6-311+G* and B3LYP/6-311+G* level, respectively) at site 3 are in good agreement with the experimental data (308 ppm and 0.56 for Ω and κ, respectively) whereas that for site 2 is unsatisfactory. Since ^{59}Co shielding constant is known to be very sensitive to the accuracy of the structural parameters,[28] we suspect that the precision of the reported crystallographic data is not of sufficient quality for reproducing the shielding tensor components with very small Ω. As shown in Table 2, additional calculations at 6-311+G(df) and 6-311++G(df) level do not improve the agreement.

Shielding Calculations of Larger Co(III) Complexes at B3PW91/6311+G* Level. Compared with $[Co(NH_3)_4CO_3]Br$ and $[Co(NH_3)_6]Cl_3$, the Co(III) systems studied in this section contain additional heavy atoms which demand a substantial increase in computational efforts. Therefore, all the calculations are carried out at the B3PW91/6-311+G* level only. The calculated results are tabulated in Table 3. It is encouraging to note that the calculated Ω and κ for $Co(acac)_3$ (1115 ppm and −0.42) agree favorably with the experimental data (1230 ppm and −0.51). For *cis*-$[Co(en)_2(NO_2)_2]Cl$, the calculated isotropic shift for *cis*-$[Co(en)_2(NO_2)_2]Cl$ (6164 ppm) agrees well with the experimental value (measured in the solid state) of *cis*-$[Co(en)_2(NO_2)_2]NO_3$ (6532 ppm). It is rather surprising to note that the calculated Ω and κ of the first and the third site of $K_3[Co(CN)_6]$ are different significantly while only one set of Ω and κ is reported for the same compound. Furthermore, the sign of the reported κ for $K_3[Co(CN)_6]$ is ambiguous. Clearly, our calculated results prompt the necessity of reexamination of $K_3[Co(CN)_6]$ experimentally.

Conclusion

In this paper, we report the first successful density functional calculation of ^{59}Co Ω and κ values for diamagnetic Co(III) complexes which agree satisfactorily with the experimental values. If medium effect of ^{59}Co chemical shifts (as large as 300 ppm[29]) is taken into consideration, the calculated isotropic chemical shifts compare favourably with the experimental values

TABLE 3: Summary of the ^{59}Co Shielding Tensors Calculated at B3PW91/6-311+G* Level[a]

complexes	σ (ppm)	δ_{calc} (ppm)	δ_{expt} (ppm)	$\delta_{calc}/\delta_{expt}$	Ω, κ (ppm)	Ω_{expt},[b] κ_{expt}[c] (ppm)
$K_3[Co(CN)_6]$ (1st site)	−5129				359, −0.19	178±10, ±(0.74±0.13)
$K_3[Co(CN)_6]$ (2nd site)	−5211				344, −0.28	178±10, ±(0.74±0.13)
$K_3[Co(CN)_6]$ (3rd site)	−4997				627, 0.52	178±10, ±(0.74±0.13)
$[Co(NH_3)_6]Cl_3$ (2nd site)	−12113	7001			64, 0.34	163, 0.66
$[Co(NH_3)_6]Cl_3$ (3rd site)	−11696	6584			243, 0.57	308, 0.56
$Co(acac)_3$	−16614	11502	12605 ± 8[c]	0.91	1115, −0.42	1230±10, −0.51±0.02
$[Co(NH_3)_4CO_3]Br$	−13886	8774	9700 ± 100[b]	0.90	1562, 0.30	1500±100, 0.33±0.19
cis-$[Co(en)_2(NO_2)_2]Cl$	−11276	6164	6532 ± 10[c,d]	0.94	783, 0.87	

[a] While all the solid-state measurements of ^{59}Co NMR chemical shifts (δ) are referenced to 0.1 M aqueous $K_3[Co(CN)_6]$, the calculated chemical shifts are referenced to the averaged calculated shielding constant (σ) of $K_3[Co(CN)_6]$. [b] The NMR data are taken from refs 30−33. [c] The details of the simulation work will be published shortly. [d] The solid-state ^{59}Co NMR data of *cis*-$[Co(en)_2(NO_2)_2]NO_3$ is taken for comparison.

($\delta_{calc}/\delta_{expt}$ ranges from 0.90 to 0.94). This achievement is anticipated to provide an impetus to the shielding calculation of other first-row transition metals.

We have also demonstrated that hybrid HF-DFT XC functional (B3PW91 and B3LYP) are more suitable for ^{59}Co shielding calculation compared to the pure density functional (BLYP). Furthermore, the results of this study show that the performance of the B3PW91 functional is slightly superior to the B3LYP functional. We suggest that B3PW91/6-311+G* or B3LYP/6-311+G* is promising for ^{59}Co shielding calculations.

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References and Notes

(1) Nakatsuji, H. In *Nuclear Magnetic Shieldings and Molecular Structure*; NATO ASI Series; Tossell, J. A., Ed.; Kluwer Academic: Amsterdam, 1993 and references therein.

(2) Tossell, J. A. *J. Phys. Chem.* **1991**, *95*, 366.

(3) Combariza, J. E.; Barfield, M.; Enemark, J. H. *J. Phys. Chem.* **1991**, *95*, 5463.

(4) Gauss, J. *Ber. Bunsen-Ges. Phys. Chem.* **1995**, *99*, 1001.

(5) Kidd, R. G. *Annu. Rep. NMR Spectrosc.* **1991**, *23*, 85.

(6) (a) Lamphun, B. N.; Webb, G. A. *J. Mol. Struct. (THEOCHEM)* **1983**, *104*, 191. (b) Xie, X.; Au-Yeung, S. C. F.; Liu, H. *J. Mol. Struct. (THEOCHEM)* **1995**, *331*, 181.

(7) *Density Functional Methods in Chemistry*; Labanowski, J. K.; Andzelm, J., Eds.; Springer-Verlag: New York, 1991.

(8) (a) Bieger, W.; Seifert, G.; Eschrig, H.; Grossmann, G. *Chem. Phys. Lett.* **1985**, *115*, 275. (b) Freier, D. A.; Fenske, R. F.; Xiao-Zeng, Y. *J. Chem. Phys.* **1985**, *83*, 3526. (c) Friedrich, K.; Seifert, G.; Grossmann, G. *Z. Phys.* **1990**, *D17*, 45. (d) Malkin, V. G.; Zhidomirov, G. M. *Zh. Strukt. Khim.* **1988**, *29*, 32. (e) Malkin, V. G.; Malkina, O. L.; Salahub, D. R. *Chem. Phys. Lett.* **1993**, *204*, 80. (f) Malkin, V. G.; Malkina, O. L.; Salahub, D. R. *Chem. Phys. Lett.* **1993**, *204*, 87. (g) Malkin, V. G.; Malkina, O. L.; Salahub, D. R. *J. Am. Chem. Soc.* **1994**, *116*, 5898. (h) Schreckenbach, G.; Ziegler, T. *J. Phys. Chem.* **1995**, *99*, 606. (i) Lee, A. M.; Handy, N. C.; Colwell, S. M. *J. Chem. Phys.* **1995**, *103*, 10095. (j) Rauhut, G.; Puyear, S.; Wolinski, K.; Pulay, P. *J. Phys. Chem.* **1996**, *100*, 6310. (k) Cheeseman, J. R.; Trucks, G. W.; Keith, T. A.; Frisch, M. J. *J. Chem. Phys.* **1996**, *104*, 5497.

(9) Note that the methods by Shreckenbach et al. use the Slater basis, while those of Rauhut et al. employ Gaussians. In contrast to the former, the latter method evaluate the Coulomb term exactly instead of using fitting functions for the Coulomb and exchange functions.

(10) (a) Chan, J. C. C.; Au-Yeung, S. C. F.; Wilson, P. J.; Webb, G. A. *J. Mol. Struct. (THEOCHEM)* **1996**, *365*, 125−130. (b) Chan, J. C. C.; Au-Yeung, S. C. F. *J. Mol. Struct. (THEOCHEM)*, in press.

(11) (a) Mason, J. *Solid State NMR* **1993**, *2*, 285. (b) Grant, D. M. In *Encyclopedia of Nuclear Magnetic Resonance*; Grant, D. M., Harris, R. K., Eds.; John Wiley & Sons: Chichester, 1996.

(12) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94, Revision B.2*; Gaussian Inc.: Pittsburgh, PA, 1995.

(13) (a) Wolinski, K.; Hilton, J. F.; Pulay, P. *J. Am. Chem. Soc.* **1990**, *112*, 8251. (b) Ditchfield, R. *Mol. Phys.* **1974**, *27*, 789.

(14) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785. (c) Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. *Chem. Phys. Lett.* **1989**, *157*, 200.

(15) Becke, A. D. *Phys. Rev.* **1988**, *A38*, 3098.

(16) Perdew, J. P.; Wang, Y. *Phys. Rev.* **1992**, *B45*, 13244.

(17) Frisch, M. J.; Frisch, A.; Foresman, J. B. *Gaussian 94 User's Reference*; Gaussian Inc.: Pittsburgh, PA, 1995.

(18) Bernal, I. *Inorg. Chim. Acta* **1985**, *96*, 99.

(19) Barclay, G. A.; Hoskins, B. F. *J. Chem. Soc.* **1962**, 586.

(20) Kruger, G. J.; Reynhardt, E. C. *Acta Crystallogr.* **1978**, *B34*, 915.

(21) Kruger, G. J.; Reynhardt, E. C. *Acta Crystallogr.* **1974**, *B30*, 822.

(22) Reynhardt, E. C. *Acta Crystallogr.* **1972**, *B28*, 524.

(23) Malli, G.; Froese, C. *Int. J. Quantum Chem.* **1967**, *1S*, 95.

(24) Hay, P. J. *J. Phys. Chem.* **1996**, *100*, 5.

(25) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623.

(26) Vanquickenborne, L. G.; Verhulst, J.; Coussens, B.; Hendrickx, M.; Pierloot, K. *J. Mol. Struct. (THEOCHEM)* **1987**, *153*, 227.

(27) Schaefer III, H. F.; Thomas, J. R.; Yamaguchi, Y.; DeLeeuw, B. J.; Vacek, G. In *Modern Electronic Structure Theory Part I*; Yarkony, D. R., Ng, C. Y., Barbara, P. F., Ceyer, S. T., Dai, H. L., Gerber, B., Valentini, J. J., Eds.; World Scientific: Singapore, 1995; p 3.

(28) Jameson, C. J.; Rehder, D.; Hoch, M. *J. Am. Chem. Soc.* **1987**, *109*, 2589.

(29) Taura, T. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 1105 and references therein.

(30) Spiess, H. W.; Hass, H.; Hartmann, H. *J. Chem. Phys.* **1969**, *50*, 3057.

(31) Reynhardt, E. C. *Solid State Commun.* **1974**, *15*, 643.

(32) Reynhardt, E. C. *J. Phys. C: Solid State Phys.* **1974**, *7*, 4135.

(33) Lourens, J. A. J.; Reynhardt, E. C. *Phys. Status Solidi A* **1972**, *11*, 739.