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On the Ground Electronic States of TiF and TiCl

Alexander I. Boldyrev and Jack Simons

Department of Chemistry, The University of Utah, Salt Lake City, Utah 84112

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The low-lying electronic states of TiF and TiCl have been studied using high level *ab initio* techniques. Both are found to have two low-lying excited electronic states, $^4\Sigma^-$ (0.080 eV (TiF) and 0.236 eV (TiCl)) and $^2\Delta$ (0.266 eV (TiF) and 0.348 eV (TiCl)), and $^4\Phi$ ground states at the highest CCSD(T)/6-311++G(2d,2f) level of theory. Our theoretical predictions of $^4\Phi$ ground electronic states for TiF and TiCl support recent experimental findings by Ram and Bernath, and our calculated bond lengths and vibrational frequencies are in reasonable agreement with their experimental data. © 1998 Academic Press

I. INTRODUCTION

The ground electronic states of TiF and TiCl have been a matter of controversy for many years. Initially, Diebner and Kay (1) interpreted the absorption spectra of TiF between 390 and 410 nm assuming a $X^4\Sigma^-$ ground electronic state. However, the $^4\Pi-^4\Sigma^-$ assignment for the transition was questioned by Shenyavskaya and Dubov (2), who reassigned the spectrum as involving $^2\Phi-^2\Delta$ and $^2\Delta-^2\Delta$ transitions and concluded that the $X^2\Delta$ state is the ground state of TiF. Most recently, Ram *et al.* (3) observed three bands in the 13 500–16 000- cm^{-1} region, with heads at 14 388, 15 033, and 15 576 cm^{-1} , which they assigned as 0–1, 0–0, and 1–0 vibrational bands of a new TiF $G^4\Phi-X^4\Phi$ transition. The assignment of $X^4\Phi$ as the ground state of TiF was consistent with unpublished theoretical calculations of Harrison and expectations based on the known ground electronic state of TiH.

Similarly for TiCl, More and Parker (4) assigned strong bands in the 400–420-nm range to a doublet transition, which Rao (5) reassigned to a $^4\Pi-^4\Sigma^-$ transition. Shenyavskaya *et al.* (6) proposed yet another assignment for the same bands, although they retained the $^4\Pi-^4\Sigma^-$ transition. Catalic, Deschamps, and Pannetier (7) and Diebner and Kay (1) made the same assignments, but Lanini (8) questioned these analyses and used rotational analysis of a few strong bands to assigned them to a $^2\Phi-^2\Delta$ transition. Phillips and Davis (9) made a rotational analysis of a number of bands in the 409.5–420-nm region and classified these bands into four doublet electronic transitions. Finally, Ram and Bernath (10) investigated the emission spectrum of TiCl in the 3000–12 000- cm^{-1} region at high resolution, and they classified the observed bands into three electronic transitions: $C^4\Delta-X^4\Phi$, $G^4\Phi-X^4\Phi$, and $G^4\Phi-C^4\Delta$. The $X^4\Phi$ state was thus assigned to the ground state of TiCl, by analogy with their work on TiF (3).

Certainly *ab initio* calculations could make a contribution in the search of the ground electronic states of the halides of Ti. We have recently successfully applied the *ab initio* quadratic CI method including single and double excited states explicitly and triple excited states by perturbation theory (QCISD(T)) to SiCu and its ions (11), as well as to ZnX diatomic molecules, where X is a first or second row atom (12). The variety of coupled cluster methods (QCISD, QCISD(T), CCSD, and CCSD(T)) offers a reasonable compromise for obtaining relatively good molecular constants for the lowest roots in every symmetry at reasonable cost. We therefore expected that our calculations of the lowest states of TiF and TiCl at the QCISD, QCISD(T), CCSD, and CCSD(T) levels of theory could help in the clarification of the problem of the ground electronic states and could indeed predict about the ground electronic states. In searches for the ground electronic states of molecules composed from even one 3d-transition metal it is very important to take into account as much dynamic correlation as possible, and the coupled cluster methods have proven to be good tools for this. Because a first-row transition element and F or Cl is involved, it is unlikely that relativistic effects need to be included if our goal is to identify the ground electronic state.

II. COMPUTATIONAL DETAILS

The bond lengths and harmonic vibrational frequencies of the lowest electronic states of TiF and TiCl having various spatial and spin multiplicities were first optimized using analytical gradients and polarized split-valence basis sets of 6-311++G(d,f) quality (13–18) (++ denotes diffuse s,p functions on F and Cl and diffuse d functions on Ti and (d,f) denotes polarization d functions on F and Cl and polarization f functions on Ti) within the second-order Møller–Plesset perturbation theory (MP2) (19) and quadratic configuration interaction methods including all single

TABLE 1
Calculated Molecular Properties of the Lowest Bound States of TiF

TiF ($^4\Phi$)	TiF ($^4\Sigma^-$)	TiF ($^2\Delta_r$)
$1\sigma^2 1\pi^4 2\sigma^2 1\delta^1 3\sigma^1 2\pi^1$	$1\sigma^2 1\pi^4 2\sigma^2 1\delta^2 3\sigma^1$	$1\sigma^2 1\pi^4 2\sigma^2 1\delta^1 3\sigma^2$
MP2/6-311++G(d,f) E PMP2=-948.169493 $R_e(\text{Ti-F})=1.867 \text{ \AA}$ $\omega_e=617 \text{ cm}^{-1}$ $\langle S^2 \rangle=3.753^a$ $T_e, \text{PMP2}=0.0 \text{ eV}$	MP2/6-311++G(d,f) E PMP2=-948.163039 $R_e(\text{Ti-F})=1.814 \text{ \AA}$ $\omega_e=665 \text{ cm}^{-1}$ $\langle S^2 \rangle=3.754^a$ $T_e, \text{PMP2}=0.176 \text{ eV}$	MP2/6-311++G(d,f) E PMP2=-948.147940 $R_e(\text{Ti-F})=1.754 \text{ \AA}$ $\omega_e=751 \text{ cm}^{-1}$ $\langle S^2 \rangle=0.791^a$ $T_e, \text{PMP2}=0.586 \text{ eV}$
QCISD/6-311++G(d,f) EQCISD=-948.177658 $R_e(\text{Ti-F})=1.867 \text{ \AA}$ $\omega_e=620 \text{ cm}^{-1}$ $\langle S^2 \rangle=3.753$ $T_e, \text{QCISD}=0.0 \text{ eV}$ QNPA(Ti)=+0.819 e QSpin(Ti)=3.005 e $\mu_e=2.958 \text{ D}$	QCISD/6-311++G(d,f) EQCISD=-948.173827 $R_e(\text{Ti-F})=1.827 \text{ \AA}$ $\omega_e=645 \text{ cm}^{-1}$ $\langle S^2 \rangle=3.754$ $T_e, \text{QCISD}=0.104 \text{ eV}$ QNPA(Ti)=+0.769 e QSpin(Ti)=3.037 e $\mu_e=3.110 \text{ D}$	QCISD/6-311++G(d,f) EQCISD=-948.165927 $R_e(\text{Ti-F})=1.770 \text{ \AA}$ $\omega_e=695 \text{ cm}^{-1}$ $\langle S^2 \rangle=0.788$ $T_e, \text{QCISD}=0.319 \text{ eV}$ QNPA(Ti)=+0.665 e QSpin(Ti)=1.036 e $\mu_e=1.863 \text{ D}$
QCISD(T)/6-311++G(2d,2f) EQCISD(T)=-948.217070 ^b $T_e, \text{QCISD(T)}=0.0 \text{ eV}$	QCISD(T)/6-311++G(2d,2f) EQCISD(T)=-948.214245 ^b $T_e, \text{QCISD(T)}=0.077 \text{ eV}$	QCISD(T)/6-311++G(2d,2f) EQCISD(T)=-948.208167 ^b $T_e, \text{QCISD(T)}=0.242 \text{ eV}$
CCSD/6-311++G(2d,2f) ECCSD=-948.206499 $R_e(\text{Ti-F})=1.872 \text{ \AA}$ $\omega_e=634 \text{ cm}^{-1}$ $\langle S^2 \rangle=3.753$ $T_e, \text{CCSD}=0.0 \text{ eV}$	CCSD/6-311++G(2d,2f) ECCSD=-948.202329 $R_e(\text{Ti-F})=1.834 \text{ \AA}$ $\omega_e=641 \text{ cm}^{-1}$ $\langle S^2 \rangle=3.754$ $T_e, \text{CCSD}=0.113 \text{ eV}$	CCSD/6-311++G(2d,2f) ECCSD=-948.191919 $R_e(\text{Ti-F})=1.779 \text{ \AA}$ $\omega_e=686 \text{ cm}^{-1}$ $\langle S^2 \rangle=0.788$ $T_e, \text{CCSD}=0.396 \text{ eV}$
CCSD(T)/6-311++G(2d,2f) ECCSD(T)=-948.216124 $R_e(\text{Ti-F})=1.869 \text{ \AA}$ $\omega_e=634 \text{ cm}^{-1}$ $\langle S^2 \rangle=3.753$ $T_e, \text{CCSD(T)}=0.0 \text{ eV}$	CCSD(T)/6-311++G(2d,2f) ECCSD(T)=-948.213191 $R_e(\text{Ti-F})=1.832 \text{ \AA}$ $\omega_e=638 \text{ cm}^{-1}$ $\langle S^2 \rangle=3.753$ $T_e, \text{CCSD(T)}=0.080 \text{ eV}$	CCSD(T)/6-311++G(2d,2f) ECCSD(T)=-948.206356 $R_e(\text{Ti-F})=1.777 \text{ \AA}$ $\omega_e=677 \text{ cm}^{-1}$ $\langle S^2 \rangle=0.783$ $T_e, \text{CCSD(T)}=0.266 \text{ eV}$

^a Spin-contamination is given before spin-projection.

^b Optimized at QCISD/6-311++G(d,f).

and double excitation (QCISD) (20). The energies of the lowest electronic states of each symmetry were then refined at the higher CCSD/6-311++G(2d,2f) and CCSD(T)/6-311++G(2d,2f) levels of theory and basis sets. The unrestricted MP2 (UMP2) wave functions for open-shell systems were spin-projected to produce purer spectroscopic states (PMP2) (21). All calculations were carried out with the GAUSSIAN 94 (22) suite of programs, and the core orbitals (F 1s, Cl 1s-2p, and Ti 1s-3p) were frozen in all correlated calculations.

III. RESULTS AND DISCUSSION

In "Periodic Table of Diatomic Molecules, Part B: Diatomics Composed from One Main Group Atom and One Transition Metal Atom" (23), we assumed the following canonical order of the *valence* molecular orbitals, $1\sigma 2\sigma-1\pi 1\delta 3\sigma 2\pi 4\sigma$, and we used the Aufbau principle to predict

the ground electronic states. According to this order of the valence MOs, one predicts the ground electronic state to be $^2\Delta_i$ ($1\sigma^2 2\sigma^2 1\pi^4 1\delta^3 3\sigma^0 2\pi^0 4\sigma^0$) for TiF, TiCl, and other valence isoelectronic halides of Ti, Zr, and Hf. One goal of the present work has been to see if those predictions are correct.

In our *ab initio* calculations we studied what are probably the three lowest electronic states: $^4\Sigma^-$ ($1\sigma^2 1\pi^4 2\sigma^2 1\delta^2 3\sigma^1-2\pi^0$), $^2\Delta_r$ ($1\sigma^2 1\pi^4 2\sigma^2 1\delta^1 3\sigma^2 2\pi^0$), and $^4\Phi$ ($1\sigma^2 1\pi^4 2\sigma^2 1\delta^1-3\sigma^1 2\pi^1$), as well as the $^2\Delta_i$ ($1\sigma^2 1\pi^4 2\sigma^2 1\delta^3 3\sigma^0 2\pi^0$) state that was expected to be the ground state on the basis of Aufbau principle. The states considered involve double occupancy of the $2s$ (1σ -MO), $2p_\sigma$ (2σ -MO), and $2p_\pi$ (1π -MO) orbitals of F, or $3s$ (1σ -MO), $3p_\sigma$ (2σ -MO), and $3p_\pi$ (1π -MO) orbitals of Cl with the three other valence electrons distributed throughout the 1δ , 3σ , and 2π valence orbitals. At the lowest level of theory (MP2) that included any correlation, the $^4\Phi$ state was found to be most stable with the

TABLE 2
Calculated Molecular Properties of the Lowest Bound States of TiCl

TiCl ($^4\Phi$)	TiCl ($^4\Sigma^-$)	TiCl ($^2\Delta_r$)
$1\sigma^2 1\pi^4 2\sigma^2 1\delta^1 3\sigma^1 2\pi^1$	$1\sigma^2 1\pi^4 2\sigma^2 1\delta^2 3\sigma^1$	$1\sigma^2 1\pi^4 2\sigma^2 1\delta^1 3\sigma^2$
MP2/6-311++G(d,f) EPMP2=-1308.138605 $R_e(\text{Ti-Cl})=2.305 \text{ \AA}$ $\omega_e=388 \text{ cm}^{-1}$ $\langle S^2 \rangle=3.753^a$ $T_e, \text{PMP2}=0.0 \text{ eV}$	MP2/6-311++G(d,f) EPMP2=-1308.123184 $R_e(\text{Ti-Cl})=2.260 \text{ \AA}$ $\omega_e=410 \text{ cm}^{-1}$ $\langle S^2 \rangle=3.755^a$ $T_e, \text{PMP2}=0.420 \text{ eV}$	MP2/6-311++G(d,f) EPMP2=-1308.092650 $R_e(\text{Ti-Cl})=2.211 \text{ \AA}$ $\omega_e=424 \text{ cm}^{-1}$ $\langle S^2 \rangle=0.760^a$ $T_e, \text{PMP2}=1.250 \text{ eV}$
QCISD/6-311++G(d,f) EQCISD=-1308.161298 $R_e(\text{Ti-Cl})=2.304 \text{ \AA}$ $\omega_e=386 \text{ cm}^{-1}$ $\langle S^2 \rangle=3.754$ $T_e, \text{QCISD}=0.0 \text{ eV}$ QNPA(Ti)=+0.744 e QSpin(Ti)=3.002 e $\mu_e=3.863 \text{ D}$	QCISD/6-311++G(d,f) EQCISD=-1308.151981 $R_e(\text{Ti-Cl})=2.336 \text{ \AA}$ $\omega_e=376 \text{ cm}^{-1}$ $\langle S^2 \rangle=3.754$ $T_e, \text{QCISD}=0.254 \text{ eV}$ QNPA(Ti)=+0.791 e QSpin(Ti)=2.968 e $\mu_e=3.868 \text{ D}$	QCISD/6-311++G(d,f) EQCISD=-1308.133503 $R_e(\text{Ti-Cl})=2.286 \text{ \AA}$ ω_e^b $\langle S^2 \rangle=0.760$ $T_e, \text{QCISD}=0.756 \text{ eV}$ QNPA(Ti)=+0.711 e QSpin(Ti)=0.980 e $\mu_e=3.168 \text{ D}$
QCISD(T)/6-311++G(2d,2f) EQCISD(T)=-1308.199740 ^c $T_e, \text{QCISD(T)}=0.0 \text{ eV}$	QCISD(T)/6-311++G(2d,2f) EQCISD(T)=-1308.190609 ^c $T_e, \text{QCISD(T)}=0.248 \text{ eV}$	QCISD(T)/6-311++G(2d,2f) EQCISD(T)=-1308.177601 ^c $T_e, \text{QCISD(T)}=0.602 \text{ eV}$
CCSD/6-311++G(2d,2f) ECCSD=-1308.191781 $R_e(\text{Ti-Cl})=2.318 \text{ \AA}$ $\omega_e=397 \text{ cm}^{-1}$ $\langle S^2 \rangle=3.755$ $T_e, \text{CCSD}=0.0 \text{ eV}$	CCSD/6-311++G(2d,2f) ECCSD=-1308.181123 $R_e(\text{Ti-Cl})=2.291 \text{ \AA}$ $\omega_e=399 \text{ cm}^{-1}$ $\langle S^2 \rangle=3.755$ $T_e, \text{CCSD}=0.290 \text{ eV}$	CCSD/6-311++G(2d,2f) ECCSD=-1308.176327 $R_e(\text{Ti-Cl})=2.324 \text{ \AA}$ ω_e^b $\langle S^2 \rangle=0.766$ $T_e, \text{CCSD}=0.421 \text{ eV}$
CCSD(T)/6-311++G(2d,2f) ECCSD(T)=-1308.199406 $R_e(\text{Ti-Cl})=2.311 \text{ \AA}$ $\omega_e=393 \text{ cm}^{-1}$ $\langle S^2 \rangle=3.755$ $T_e, \text{CCSD(T)}=0.0 \text{ eV}$	CCSD(T)/6-311++G(2d,2f) ECCSD(T)=-1308.190699 $R_e(\text{Ti-Cl})=2.288 \text{ \AA}$ $\omega_e=398 \text{ cm}^{-1}$ $\langle S^2 \rangle=3.755$ $T_e, \text{CCSD(T)}=0.236 \text{ eV}$	CCSD(T)/6-311++G(2d,2f) ECCSD(T)=-1308.186602 $R_e(\text{Ti-Cl})=2.336 \text{ \AA}$ ω_e^b $\langle S^2 \rangle=0.766$ $T_e, \text{CCSD(T)}=0.348 \text{ eV}$

^a Spin-contamination is given before spin-projection.

^b Frequency was not calculated at this level of theory due to convergence problems.

^c Optimized at QCISD/6-311++G(d,f).

$^4\Sigma^-$ and $^2\Delta_r$ states being higher in energy than the ground electronic state by 0.176 eV ($^4\Sigma^-$) and 0.586 eV ($^2\Delta_r$) for TiF and by 0.420 eV ($^4\Sigma^-$) and 1.250 eV ($^2\Delta_r$) for TiCl. The $^2\Delta_i$ state was found to be substantially higher in energy (3.51 eV for TiF and 3.46 eV for TiCl), therefore the $^2\Delta_i$ state was excluded from further examination.

The three lowest electronic states, $^4\Phi$ ($1\sigma^2 1\pi^4 2\sigma^2 1\delta^1 3\sigma^1 2\pi^1$), $^4\Sigma^-$ ($1\sigma^2 1\pi^4 2\sigma^2 1\delta^2 3\sigma^1 2\pi^0$), and $^2\Delta_r$ ($1\sigma^2 1\pi^4 2\sigma^2 1\delta^1 3\sigma^2 2\pi^0$), were then studied at the QCISD, QCISD(T), CCSD, and CCSD(T) levels of theory. The results of our calculations for TiF and TiCl are presented in Table 1 and Table 2, respectively.

The $^4\Phi$ state was found to be the ground state at all (MP2, QCISD, QCISD(T), CCSD, and CCSD(T)) levels of theory for both TiF and TiCl, in agreement with recent experimental findings (3, 10) and similar to what is known for TiH (24–27). The MP2, QCISD, CCSD, and CCSD(T)

methods give very similar bond lengths (1.867–1.872 Å for TiF and 2.304–2.318 Å for TiCl) and harmonic frequencies (617–634 cm^{-1} for TiF and 386–397 cm^{-1} for TiCl). These numbers compare reasonably with the experimental values: $R_e(\text{TiF}) = 1.8311 \text{ \AA}$ and $\Delta G_{1/2} = 650.70 \text{ cm}^{-1}$ for TiF [3], and $R_e(\text{TiCl}) = 2.2647 \text{ \AA}$ and $\Delta G_{1/2} = 404.33 \text{ cm}^{-1}$ for TiCl [10]. In the $^4\Phi$ state, we find the unpaired spin density to be located completely on the Ti atom, and we find the charge density to be very ionic (atomic effective charges: $Q(\text{Ti}) = +0.82 \text{ e}$ for TiF and $Q(\text{Ti}) = +0.74 \text{ e}$ for TiCl which produce dipole moments of $\mu_e(\text{TiF}) = 2.96 \text{ D}$ and $\mu_e(\text{TiCl}) = 3.86 \text{ D}$).

The $^4\Sigma^-$ state arising from promoting one electron from the 2π -MO into the 1δ -MO is the lowest excited state for both molecules with 0.080 eV (TiF) and 0.236 eV (TiCl) excitation energies at the CCSD(T)/6-311++G(2d,2f) level of theory. This state has a higher dipole moment (μ_e

= 3.11 D for TiF and $\mu_e = 3.87$ D for TiCl) than the ground state and has all of the unpaired electron density located on the Ti atom.

The $^2\Delta$ doublet state arising from promotion of one electron from the 2π -MO into the 3σ -MO is on a somewhat higher (0.266 eV (TiF) and 0.348 eV (TiCl) at the CCSD(T)/6-311++G(2d,2f) level and is less ionic (atomic effective charges: $Q(\text{Ti}) = 0.67$ e for TiF and $Q(\text{Ti}) = 0.71$ e for TiCl and dipole moments: $\mu_e(\text{TiF}) = 1.86$ and $\mu_e(\text{TiCl}) = 3.17$ D).

In their $^4\Phi$ ground states, both TiF and TiCl are strongly bound with dissociation energies of $D_e(\text{TiF}) = 5.36$ eV, $D_0(\text{TiF}) = 5.32$ eV, $D_e(\text{TiCl}) = 3.98$ eV, and $D_0(\text{TiCl}) = 3.93$ eV (all at the CCSD(T)/6-311++G(2d,2f) level of theory).

IV. SUMMARY

Our theoretical predictions of $^4\Phi$ ground electronic states for TiF and TiCl support recent experimental findings by Ram and Bernath (3, 10). Our calculated bond lengths and vibrational frequencies at the CCSD(T)/6-311++G(2d,2f) level of theory are in decent agreement with their experimental data. The high-spin ground electronic $^4\Phi$ states of TiF and TiCl are not the $^2\Delta_i$ ground electronic states expected from Aufbau principle.

We found a reasonable agreement among the results obtained for all the low-lying states of TiF and TiCl at the four coupled cluster methods (QCISD, QSCISD(T), CCSD, and CCSD(T)). In our previous calculations on AlZn (12), we found important contributions from triple excitations (e.g., going from QCISD to QSCISD(T)), but for TiF and TiCl triple excitations were found to make only modest contributions to the molecular constants.

The three lowest states are very close in energy for TiF at our highest level of theory but are more widely spaced for TiCl. One could then speculate that for the less ionic TiBr and TiI, the $^4\Phi$ state should be even more stable relative to the other states and should thus be the ground state again. Ram and Bernath (28) recently studied ZrCl and found evidence that suggests the $^4\Phi$ state is also the ground electronic state for that molecule. Based on results of our calculations and the recent experimental data by Ram and Bernath, the previously proposed ground electronic states for all halides of Ti, Zr, and Hf should therefore be reconsidered.

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REFERENCES

1. R. L. Diebner and J. G. Kay, *J. Chem. Phys.* **51**, 3547–3554 (1969).
2. E. A. Shenyavskaya and V. M. Dubov, *J. Mol. Spectrosc.* **113**, 85–92 (1985).
3. R. S. Ram, J. R. D. Peers, Y. Teng, A. G. Adam, A. Muntianu, P. F. Bernath, and S. P. Davis, *J. Mol. Spectrosc.* **184**, 186–204 (1997).
4. K. R. More and A. H. Parker, *Phys. Rev.* **52**, 1150–1152 (1937).
5. V. R. Rao, *Ind. J. Phys.* **23**, 535–546 (1949).
6. E. A. Shenyavskaya, Y. Y. Kuzyakov, and V. M. Tatevskii, *Opt. Spectrosc.* **12**, 197–199 (1962).
7. A. Catalic, P. Deschamps, and G. Pannetier, *C. R. Acad. Soc. Paris*, **270**, 146–149 (1970).
8. K. P. Lanini, Ph.D. Dissertation, University of Michigan, Ann Arbor, Michigan, 1972.
9. J. G. Phillips and S. P. Davis, *Astrophys. J. Suppl. Ser.* **71**, 163–172 (1989).
10. R. S. Ram and P. F. Bernath, *J. Mol. Spectrosc.* **186**, 113–130 (1997).
11. A. I. Boldyrev, J. Simons, J. J. Scherer, J. B. Paul, C. P. Collier, and R. J. Saykally, *J. Chem. Phys.* **108**, N14 (1998).
12. A. I. Boldyrev and J. Simons, *Mol. Phys.* **92**, 365–379 (1997).
13. A. D. McLean and G. S. Chandler, *J. Chem. Phys.* **72**, 5639–5648 (1980).
14. R. Krishnan, J. S. Binkley, R. Seeger, and J. A. Pople, *J. Chem. Phys.* **72**, 650–654 (1980).
15. A. J. H. Wachters, *J. Chem. Phys.* **52**, 1033–1036 (1970).
16. P. J. Hay, *J. Chem. Phys.* **66**, 4377–4384 (1977).
17. K. Raghavachari and G. W. Trucks, *J. Chem. Phys.* **91**, 1062–1065 (1989).
18. T. H. Dunning, Jr. and P. J. Hay, in "Modern Theoretical Chemistry," (H. F. Schaefer, III, Ed.), pp. 1–28, Plenum, New York, 1976.
19. J. A. Pople, R. Seeger, and R. Krishnan, *Int. J. Quant. Chem. Symp.* **11**, 149–163 (1977).
20. J. A. Pople, M. Head-Gordon, and K. Raghavachari, *J. Chem. Phys.* **87**, 5968–5975 (1987).
21. H. B. Schlegel, *J. Chem. Phys.* **84**, 4530–4534 (1984).
22. Gaussian 94 (revision A.1). M. J. Frisch, G. M. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. A. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. J. P. Stewart, M. Head-Gordon, C. Gonzales, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 1995.
23. A. I. Boldyrev and J. Simons, "Periodic Table of Diatomic Molecules. Part B: Diatomics Composed of One Main Group Element and One Transition Metal Atom," Wiley & Sons Publisher, London, 1997.
24. T. C. Steimle, J. E. Shirley, B. Simard, M. Vasseur, and P. Hackett, *J. Chem. Phys.* **95**, 7179–7182 (1991).
25. O. Launila and B. Lindgren, *J. Chem. Phys.* **104**, 6418–6422 (1996).
26. C. W. Bauschlicher, Jr., *J. Phys. Chem.* **92**, 3020–3023 (1988).
27. J. Anglada, P. J. Bruna, and S. D. Peyerimhoff, *Mol. Phys.* **69**, 281–303 (1990).
28. R. S. Ram and P. F. Bernath, *J. Mol. Spectrosc.*, in press.