

Ab initio study of the bonding of zinc atoms to first- and second-row main group atoms

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A systematic *ab initio* study has been made of the bonding between Zn atoms and all first- and second-row main group atoms. Ground state term symbols, equilibrium bond lengths, vibrational frequencies and dissociation energies have been determined, and the nature of the bonding (van der Waals, dative and chemical) has been examined.

1. Introduction

Zinc has a closed shell ($1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10}$) electronic configuration in its ground state and does not have a positive electron affinity [1]. Therefore, bonding to other atoms (forming XZn) is expected to occur either when zinc is promoted to $4s^1 4p^1$ or when dative bonding from Zn to X is favoured. Thus XZn is expected to be thermodynamically stable only if the Zn ($4s^1 4p^1$)—X intrinsic bond energy is larger than the promotion energy ($\Delta E(^1S-^3P) = 4.038$ eV [2]) or if the electron affinity of the X atom is high enough to make dative charge transfer from Zn to X (IP(Zn) = 9.391 eV [2]) significant. Hence, one expects Zn to form only weak van der Waals complexes with electropositive atoms and relatively stable chemically bound diatomic molecules with the more electronegative atoms.

In this work, we have undertaken an *ab initio* study of all diatomic molecules composed of Zn and a first- or second-row main group atom. In doing so we wanted to learn how the bonding evolves from van der Waals complexes to more chemically bound diatomics. It should be stressed that data on diatomics composed of a transition metal atom and a main group element are scarce [3, 4]. Huber and Herzberg quote only OZn, SZn, FZn and ClZn in their book on molecular constants [5]. In *Spectroscopic References for Diatomic Molecules* [4], references on experimental and theoretical data are available only for LiZn [6–8], NaZn [8, 9], AlZn [10], OZn [11–21], SZn [16, 22–24], FZn [25, 26], ClZn [25, 27] and ArZn [28–32]. Thus, even the ground electronic states and basic molecular constants are not yet known for most of the XZn (X = Li–Ne, Na–Ar) molecules. Hence, another goal of our work was to establish the ground electronic states for all XZn (X = Li–Ne, Na–Ar) diatomic molecules, to predict their molecular properties (bond lengths, dissociation energies, vibrational

frequencies, etc.) and to characterize the bonding in these molecules.

2. Computational details

The bond lengths and harmonic vibrational frequencies of the lowest electronic states of LiZn, NaZn, BeZn, MgZn, BZn, AlZn, CZn, SiZn, NZn, PZn, OZn, SZn, FZn, ClZn, NeZn and ArZn were optimized using analytical gradients and polarized split-valence basis sets of 6-311++G(d,f) quality [33–38] (where ++ denotes diffuse s,p functions on the main group atoms and diffuse d functions on Zn and (d, f) denotes polarization d functions on the main group atom and polarization f functions on Zn) within density functional theory (B3LYP) [39, 40], second-order Møller–Plesset perturbation theory (MP2) [41] and quadratic configuration interaction methods including all single and double excitations (QCISD) [42]. The energies of the lowest states were then refined at the QCISD(T)/6-311++G(2d, 2f) level using the QCISD/6-311++G(d, f) optimized geometries. The unrestricted MP2 (UMP2) wavefunctions for open shell systems were spin-projected to produce pure spectroscopic states (PMP2) [43]. All calculations were carried out with the Gaussian 94 [44] suite of programs and core orbitals were kept frozen (the Zn d electrons were not frozen) in all correlated calculations.

3. Results and discussion

For all of these diatomics we considered only the highest spin multiplicity states for each MO occupancy because the high-spin state is always lower in energy. This is acceptable because our goal was to identify the ground electronic states.

3.1. *LiZn and NaZn*

Potential energy curves for the lowest several states of LiZn [6] and NaZn [8] have been studied previously at the MRDCI level of theory with relatively large basis sets. A $2^2\Sigma^+$ state was found to be the ground state for both molecules. The $2^2\Sigma^+$ excited state was found to be 11450.9 cm^{-1} (LiZn) and 13906.8 cm^{-1} (NaZn) above the ground state. The excitation energy from the ground electronic state into the lowest excited state $1^2\Pi$ was found to be 7059.7 cm^{-1} (LiZn) and 9607.2 cm^{-1} (NaZn). Therefore, the $X^2\Sigma^+$ ground electronic states are well established.

The ground electronic state is a van der Waals complex with a long ($R_e = 2.926\text{ \AA}$ for LiZn and $R_e = 3.413\text{ \AA}$ for NaZn) bond, low dissociation energy ($D_e = 0.163\text{ eV}$ for LiZn and $D_e = 0.103\text{ eV}$ for NaZn) and low vibrational frequency ($\omega_e = 126.6\text{ cm}^{-1}$ for LiZn and $\omega_e = 75.1\text{ cm}^{-1}$ for NaZn). By contrast, both the $2^2\Sigma^+$ and $1^2\Pi$ excited states were found to be substantially more strongly bound with respect to the corresponding adiabatic dissociation limits ($D_e = 0.588\text{ eV}$ for $2^2\Sigma^+$ and $D_e = 1.138\text{ eV}$ for $1^2\Pi$ for LiZn and $D_e = 0.426\text{ eV}$ for $2^2\Sigma^+$ and $D_e = 0.956\text{ eV}$ for $1^2\Pi$ for NaZn) and to have shorter bond lengths ($R_e = 2.696\text{ \AA}$ for $2^2\Sigma^+$ and $R_e = 2.425\text{ \AA}$ for $1^2\Pi$ for LiZn and $R_e = 2.916\text{ \AA}$ for $2^2\Sigma^+$ and $R_e = 2.672\text{ \AA}$ for $1^2\Pi$ for NaZn). In both of these states there is significant charge transfer, and the configurations ($1\sigma^2 2\sigma^2 1\pi^4 1\delta^4 3\sigma^0 4\sigma^1$ and $1\sigma^2 2\sigma^2 1\pi^4 1\delta^4 3\sigma^0 2\pi^1$) reflect significant $\text{Zn}^+ \text{Li}^-$ or $\text{Zn}^+ \text{Na}^-$ dative character, because the previously occupied $2s$ or $3s$ orbital is empty, thus allowing $\text{Zn } 4s^2 \rightarrow \text{Li } 2s$ (or $\text{Na } 3s$) dative bonding to occur.

We studied only the ground $2^2\Sigma^+$ ($1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^1$) electronic states for LiZn and NaZn at the B3LYP, MP2 and QCISD levels of theory, and the results of our calculations are presented in table 1. Here, the 1σ , 1δ and 1π MOs are primarily Zn $3d$, the 2σ MO is Zn $4s$, and the 3σ MO is Li $2s$ or Na $3s$. Our findings vary dramatically among the DFT (B3LYP), MP2 and QCISD methods. Surprisingly, B3LYP results are in the best agreement with the MRDCI data obtained by Milosevic *et al.* [6] and Azinovic *et al.* [8]. Our QCISD data for LiZn still are very close and those for NaZn are somewhat further off when compared with the MRDCI data. However, taking into account the weak bonds and very soft potentials, we consider this agreement as fair. Our data at the MP2 level are significantly incorrect, which we believe is because of the poor description of the atomic polarizabilities at this level of theory. Finally, only a small charge transfer was found in the ground electronic states of LiZn and NaZn, as a result of which these molecules have very small dipole moments.

Table 1. Calculated molecular properties of LiZn and NaZn.

LiZn ($2^2\Sigma^+$) $1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^1 2\pi^0$	NaZn ($2^2\Sigma^+$) $1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^1 2\pi^0$
B3LYP/6-311++G(d, f) $E_{\text{B3LYP}} = -1786.850108$ $R_e(\text{Li-Zn}) = 2.940\text{ \AA}$ $\omega_e = 161\text{ cm}^{-1}$ $\langle S^2 \rangle = 0.752^a$	B3LYP/6-311++G(d, f) $E_{\text{B3LYP}} = -1941.643328$ $R_e(\text{Na-Zn}) = 3.356\text{ \AA}$ $\omega_e = 74\text{ cm}^{-1}$ $\langle S^2 \rangle = 0.752^a$
MP2/6-311++G(d, f) $E_{\text{MP2}} = -1785.525870$ $R_e(\text{Li-Zn}) = 3.732\text{ \AA}$ $\omega_e = 33\text{ cm}^{-1}$ $\langle S^2 \rangle = 0.766^a$	MP2/6-311++G(d, f) $E_{\text{MP2}} = -1939.939211$ $R_e(\text{Na-Zn}) = 4.388\text{ \AA}$ $\omega_e = 19\text{ cm}^{-1}$ $\langle S^2 \rangle = 0.754^a$
QCISD/6-311++G(d, f) $E_{\text{QCISD}} = -1785.498440$ $R_e(\text{Li-Zn}) = 3.092\text{ \AA}$ $\omega_e = 115\text{ cm}^{-1}$ $\langle S^2 \rangle = 0.796^a$ $Q^{\text{Mull}}(\text{Li}) = +0.040e$ $Q^{\text{NPA}}(\text{Li}) = +0.003e$ $Q^{\text{Spin}}(\text{Li}) = +0.885e$ $\mu_e = 0.074\text{ D}$	QCISD/6-311++G(d, f) $E_{\text{QCISD}} = -1939.911021$ $R_e(\text{Na-Zn}) = 3.737\text{ \AA}$ $\omega_e = 35\text{ cm}^{-1}$ $\langle S^2 \rangle = 0.768^a$ $Q^{\text{Mull}}(\text{Na}) = +0.023e$ $Q^{\text{NPA}}(\text{Na}) = +0.003e$ $Q^{\text{Spin}}(\text{Na}) = +0.954e$ $\mu_e = 0.008\text{ D}$
QCISD(T)/6-311++G(2d, 2f) $E_{\text{QCISD(T)}} = -1785.575489$ $R(\text{Li-Zn}) = 3.092\text{ \AA}^b$	QCISD(T)/6-311++G(2d, 2f) $E_{\text{QCISD(T)}} = -1939.987983$ $R(\text{Na-Zn}) = 3.737\text{ \AA}^b$

^a Here and in other tables the spin contamination is given before spin projection.

^b At QCISD/6-311++G(d, f) optimal geometry.

3.2. *BeZn and MgZn*

There are no experimental or theoretical data on these molecules in the literature according to the *Spectroscopic References for Diatomic Molecules* [4]. We studied four low-lying electronic states, $1^1\Sigma^+$ ($1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^2 2\pi^0$), $3^1\Pi$ ($1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^1 2\pi^1$), $3^1\Sigma^+$ ($1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^1 2\pi^0 4\sigma^1$) and $3^1\Sigma^-$ ($1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^0 2\pi^2$), which were derived assuming double occupancy for the $3d$ electrons of Zn, as well as for the lowest Zn $4s$ 2σ MO and distributing the two other valence electrons throughout the 3σ , 4σ and 2π valence orbitals (the lowest excitation energies of Be (2.72 eV [2]) and Mg (2.71 eV [2]) are lower than Zn $4s^2 4p^0 - 4s^2 4p^1$ (4.04 eV [2]) energy gap, so the lowest states of BeZn and MgZn should keep Zn $4s^2$ occupancy).

The $1^1\Sigma^+$ state was found to be the ground state at all three (B3LYP, MP2 and QCISD) levels of theory for both BeZn and MgZn, but again all three methods give very different bond lengths, harmonic frequencies and dissociation energies for this state (see tables 2 and 3). We believe that our bond lengths and harmonic frequencies at the QCISD/6-311++G(d, f) level and bond energies at the QCISD(T)/6-311++G(2d, 2f) level provide the most reasonable estimates.

Table 2. Calculated molecular properties of the lowest BeZn states.

BeZn ($^1\Sigma^+$) $1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^2 2\pi^0$	BeZn ($^3\Pi_r$) $1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^1 2\pi^1$	BeZn ($^3\Sigma^+$) $1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^1 2\pi^0 4\sigma^1$	BeZn ($^3\Sigma^-$) $1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^0 2\pi^2$
B3LYP/6-311++G(d, f) $E_{B3LYP} = -1794.025894$ $R_c(\text{Be-Zn}) = 3.037 \text{ \AA}$ $\omega_e = 84 \text{ cm}^{-1}$	B3LYP/6-311++G(d, f) $E_{B3LYP} = -1793.971747$ $R_c(\text{Be-Zn}) = 2.207 \text{ \AA}$ $\omega_e = 428 \text{ cm}^{-1}$ $\langle S^2 \rangle = 2.010$	B3LYP/6-311++G(d, f) $E_{B3LYP} = -1793.967056$ $R_c(\text{Be-Zn}) = 2.374 \text{ \AA}$ $\omega_e = 378 \text{ cm}^{-1}$ $\langle S^2 \rangle = 2.003$	B3LYP/6-311++G(d, f) $E_{B3LYP} = -1793.900144$ $R_c(\text{Be-Zn}) = 1.985 \text{ \AA}$ $\omega_e = 612 \text{ cm}^{-1}$ $\langle S^2 \rangle = 2.032$
$T_{e,B3LYP} = 0.0 \text{ eV}$	$T_{e,B3LYP} = 1.473 \text{ eV}$	$T_{e,B3LYP} = 1.601 \text{ eV}$	$T_{e,B3LYP} = 3.422 \text{ eV}$
MP2/6-311++G(d, f) $E_{PMP2} = -1792.691943$ $R_c(\text{Be-Zn}) = 3.870 \text{ \AA}$ $\omega_e = 33 \text{ cm}^{-1}$	MP2/6-311++G(d, f) $E_{PMP2} = -1792.637463$ $R_c(\text{Be-Zn}) = 2.186 \text{ \AA}$ $\omega_e = 444 \text{ cm}^{-1}$ $\langle S^2 \rangle = 2.123$	MP2/6-311++G(d, f) $E_{PMP2} = -1792.638507$ $R_c(\text{Be-Zn}) = 2.334 \text{ \AA}$ $\omega_e = 420 \text{ cm}^{-1}$ $\langle S^2 \rangle = 2.011$	MP2/6-311++G(d, f) $E_{PMP2} = -1792.562959$ $R_c(\text{Be-Zn}) = 1.940 \text{ \AA}$ $\omega_e = 660 \text{ cm}^{-1}$ $\langle S^2 \rangle = 2.307$
$T_{e,PMP2} = 0.0 \text{ eV}$	$T_{e,PMP2} = 1.482 \text{ eV}$	$T_{e,PMP2} = 1.454 \text{ eV}$	$T_{e,PMP2} = 3.510 \text{ eV}$
QCISD/6-311++G(d, f) $E_{QCISD} = -1792.681444$ $R_c(\text{Be-Zn}) = 4.801 \text{ \AA}$ $\omega_e = 20 \text{ cm}^{-1}$	QCISD/6-311++G(d, f) $E_{QCISD} = -1792.614357$ $R_c(\text{Be-Zn}) = 2.227 \text{ \AA}$ $\omega_e = 427 \text{ cm}^{-1}$ $\langle S^2 \rangle = 2.126$	QCISD/6-311++G(d, f) $E_{QCISD} = -1792.613780$ $R_c(\text{Be-Zn}) = 2.365 \text{ \AA}$ $\omega_e = 403 \text{ cm}^{-1}$ $\langle S^2 \rangle = 2.011$	QCISD/6-311++G(d, f) $E_{QCISD} = -1792.541694$ $R_c(\text{Be-Zn}) = 1.994 \text{ \AA}$ $\omega_e = 617 \text{ cm}^{-1}$ $\langle S^2 \rangle = 2.348$
$T_{e,QCISD} = 0.0 \text{ eV}$ $Q^{\text{Mull}}(\text{Be}) = +0.003 e$ $Q^{\text{NPA}}(\text{Be}) = +0.000 e$	$T_{e,QCISD} = 1.825 \text{ eV}$ $Q^{\text{Mull}}(\text{Be}) = -0.062 e$ $Q^{\text{NPA}}(\text{Be}) = -0.094 e$ $Q^{\text{Spin}}(\text{Be}) = +0.362 e$	$T_{e,QCISD} = 1.841 \text{ eV}$ $Q^{\text{Mull}}(\text{Be}) = +0.073 e$ $Q^{\text{NPA}}(\text{Be}) = -0.056 e$ $Q^{\text{Spin}}(\text{Be}) = +1.143 e$	$T_{e,QCISD} = 3.803 \text{ eV}$ $Q^{\text{Mull}}(\text{Be}) = -0.148 e$ $Q^{\text{NPA}}(\text{Be}) = -0.107 e$ $Q^{\text{Spin}}(\text{Be}) = +1.448 e$
$\mu_e = 0.003 \text{ D}$	$\mu_e = 1.325 \text{ D}$	$\mu_e = 0.164 \text{ D}$	$\mu_e = 0.848 \text{ D}$
QCISD(T)/6-311++G(2d, 2f) $E_{QCISD(T)} = -1792.758137$ $R(\text{Be-Zn}) = 4.801 \text{ \AA}^a$ $T_{e,QCISD(T)} = 0.0 \text{ eV}$	QCISD(T)/6-311++G(2d, 2f) $E_{QCISD(T)} = -1792.693217$ $R(\text{Be-Zn}) = 2.227 \text{ \AA}^a$ $T_{e,QCISD(T)} = 1.767 \text{ eV}$	QCISD(T)/6-311++G(2d, 2f) $E_{QCISD(T)} = -1792.689726$ $R(\text{Be-Zn}) = 2.365 \text{ \AA}^a$ $T_{e,QCISD(T)} = 1.861 \text{ eV}$	QCISD(T)/6-311++G(2d, 2f) $E_{QCISD(T)} = -1792.621322$ $R(\text{Be-Zn}) = 1.994 \text{ \AA}^a$ $T_{e,QCISD(T)} = 3.723 \text{ eV}$

^a At QCISD/6-311++G(d, f) optimal geometry.

The high-spin $^3\Pi_r$ and $^3\Sigma^+$ (with $^3P(2s^1 2p^1, \text{Be}; 3s^1 3p^1, \text{Mg}) + ^1S(\text{Zn})$ asymptote) and $^3\Sigma^-$ (with $^3P(2p^2, \text{Be}; 3p^2, \text{Mg}) + ^1S(\text{Zn})$ asymptote) states arising from promoting one or two electrons from the Be or Mg dominated 3σ MO into the 2π MO or/and the 4σ MO (both of which Be or Mg dominated) were found to be substantially higher in energy than the ground electronic state. The bond lengths and frequencies of the $^3\Pi_r$ and $^3\Sigma^+$ states, where just one electron is promoted into the 4σ MO or 2π MO, are close to each other, while the corresponding numbers for the $^3\Sigma^-$ state, where two electrons are promoted into the 2π MO, are shorter and higher, respectively. Very little charge transfer was found to have occurred for all the excited states of BeZn and MgZn. Our calculated intrinsic bond energies for the two lowest excited states were found to be: 1.09 eV ($^3\Pi_r$, BeZn); 1.00 eV ($^3\Sigma^+$, BeZn); 0.75 eV ($^3\Pi_r$, MgZn) and 0.58 eV ($^3\Sigma^+$, MgZn). Clearly, these intrinsic bond energies for the triplet states are not able to overcome the excitation energies of Be (2.85 eV at QCISD(T)/6-

311++G(2d, 2f), 2.72 eV experiment [2]) or of Mg (2.70 eV at QCISD(T)/6-311++G(2d, 2f), 2.71 eV experiment [2]), as a result of which the singlet $^1\Sigma^+$ state with a weak van der Waals bond remains the ground state.

3.3. BZn and AlZn

The only known work on these molecules is the spectroscopic work on AlZn published by Morse and co-workers [10]. The $X^2\Pi_r$ ground electronic state for AlZn was established in these experiments and found to have an equilibrium bond length $r_0(\text{Al-Zn}) = 2.6957(4) \text{ \AA}$ and a vibrational frequency $\Delta G_{1/2} = 153.4(7) \text{ cm}^{-1}$. Two excited A ($\Omega = 0.5$) and B $^2\Pi_r$ states have been observed in these experiments with excitation energies of 17870 cm^{-1} and 18550 cm^{-1} , respectively.

Boron and aluminium atoms have $2s^2 2p^1$ (B) and $3s^2 3p^1$ (Al) valence electronic configurations, and without electronic excitation one expects only a weak van der Waals bond with the zinc atom producing

Table 3. Calculated molecular properties of the lowest MgZn states.

MgZn ($^1\Sigma^+$) $1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^2 2\pi^0$	MgZn ($^3\Pi_f$) $1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^1 2\pi^1$	MgZn ($^3\Sigma^+$) $1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^1 2\pi^0 4\sigma^1$	MgZn ($^3\Sigma^-$) $1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^0 2\pi^2$
B3LYP/6-311++G(d, f) $E_{B3LYP} = -1979.447\ 037$ $R_e(\text{Mg-Zn}) = 3.839 \text{ \AA}$ $\omega_e = 28 \text{ cm}^{-1}$	B3LYP/6-311++G(d, f) $E_{B3LYP} = -1979.372\ 379$ $R_e(\text{Mg-Zn}) = 2.600 \text{ \AA}$ $\omega_e = 228 \text{ cm}^{-1}$ $\langle S^2 \rangle = 2.007$	B3LYP/6-311++G(d, f) $E_{B3LYP} = -1979.366\ 408$ $R_e(\text{Mg-Zn}) = 2.832 \text{ \AA}$ $\omega_e = 186 \text{ cm}^{-1}$ $\langle S^2 \rangle = 2.002$	B3LYP/6-311++G(d, f) $E_{B3LYP} = -1979.286\ 309$ $R_e(\text{Mg-Zn}) = 2.332 \text{ \AA}$ $\omega_e = 336 \text{ cm}^{-1}$ $\langle S^2 \rangle = 2.010$
$T_{e,B3LYP} = 0.0 \text{ eV}$	$T_{e,B3LYP} = 2.031 \text{ eV}$	$T_{e,B3LYP} = 2.194 \text{ eV}$	$T_{e,B3LYP} = 4.373 \text{ eV}$
MP2/6-311++G(d, f) $E_{PMP2} = -1977.722\ 088$ $R_e(\text{Mg-Zn}) = 4.150 \text{ \AA}$ $\omega_e = 26 \text{ cm}^{-1}$	MP2/6-311++G(d, f) $E_{PMP2} = -1977.655\ 118$ $R_e(\text{Mg-Zn}) = 2.589 \text{ \AA}$ $\omega_e = 234 \text{ cm}^{-1}$ $\langle S^2 \rangle = 2.098$	MP2/6-311++G(d, f) $E_{PMP2} = -1977.651\ 435$ $R_e(\text{Mg-Zn}) = 2.780 \text{ \AA}$ $\omega_e = 211 \text{ cm}^{-1}$ $\langle S^2 \rangle = 2.011$	MP2/6-311++G(d, f) $E_{PMP2} = -1977.569\ 056$ $R_e(\text{Mg-Zn}) = 2.283 \text{ \AA}$ $\omega_e = 376 \text{ cm}^{-1}$ $\langle S^2 \rangle = 2.201$
$T_{e,PMP2} = 0.0 \text{ eV}$	$T_{e,PMP2} = 1.822 \text{ eV}$	$T_{e,PMP2} = 1.922 \text{ eV}$	$T_{e,PMP2} = 4.164 \text{ eV}$
QCISD/6-311++G(d, f) $E_{QCISD} = -1977.704\ 258$ $R_e(\text{Mg-Zn}) = 4.893 \text{ \AA}$ $\omega_e = 15 \text{ cm}^{-1}$	QCISD/6-311++G(d, f) $E_{QCISD} = -1977.630\ 209$ $R_e(\text{Mg-Zn}) = 2.636 \text{ \AA}$ $\omega_e = 220 \text{ cm}^{-1}$ $\langle S^2 \rangle = 2.099$	QCISD/6-311++G(d, f) $E_{QCISD} = -1977.625\ 979$ $R_e(\text{Mg-Zn}) = 2.817 \text{ \AA}$ $\omega_e = 202 \text{ cm}^{-1}$ $\langle S^2 \rangle = 2.011$	QCISD/6-311++G(d, f) $E_{QCISD} = -1977.546\ 769$ $R_e(\text{Mg-Zn}) = 2.350 \text{ \AA}$ $\omega_e = 340 \text{ cm}^{-1}$ $\langle S^2 \rangle = 2.247$
$T_{e,QCISD} = 0.0 \text{ eV}$ $Q^{\text{Mull}}(\text{Mg}) = +0.003 e$ $Q^{\text{NPA}}(\text{Mg}) = +0.000 e$	$T_{e,QCISD} = 2.015 \text{ eV}$ $Q^{\text{Mull}}(\text{Mg}) = +0.082 e$ $Q^{\text{NPA}}(\text{Mg}) = +0.112 e$ $Q^{\text{Spin}}(\text{Mg}) = 1.415 e$	$T_{e,QCISD} = 2.130 \text{ eV}$ $Q^{\text{Mull}}(\text{Mg}) = +0.243 e$ $Q^{\text{NPA}}(\text{Mg}) = +0.143 e$ $Q^{\text{Spin}}(\text{Mg}) = 1.205 e$	$T_{e,QCISD} = 4.285 \text{ eV}$ $Q^{\text{Mull}}(\text{Mg}) = +0.081 e$ $Q^{\text{NPA}}(\text{Mg}) = +0.211 e$ $Q^{\text{Spin}}(\text{Mg}) = 1.268 e$
$\mu_e = 0.004 \text{ D}$	$\mu_e = 1.149 \text{ D}$	$\mu_e = 1.257 \text{ D}$	$\mu_e = 1.828 \text{ D}$
QCISD/6-311++G(2d, 2f) $E_{QCISD(T)} = -1977.781\ 070$ $R(\text{Be-Zn}) = 4.893 \text{ \AA}^a$ $T_{e,QCISD(T)} = 0.0 \text{ eV}$	QCISD/6-311++G(2d, 2f) $E_{QCISD(T)} = -1977.709\ 035$ $R(\text{Be-Zn}) = 2.636 \text{ \AA}^a$ $T_{e,QCISD(T)} = 1.960 \text{ eV}$	QCISD/6-311++G(2d, 2f) $E_{QCISD(T)} = -1977.702\ 492$ $R(\text{Mg-Zn}) = 2.817 \text{ \AA}^a$ $T_{e,QCISD(T)} = 2.138 \text{ eV}$	QCISD/6-311++G(2d, 2f) $E_{QCISD(T)} = -1977.626\ 661$ $R(\text{Mg-Zn}) = 2.350 \text{ \AA}^a$ $T_{e,QCISD(T)} = 4.201 \text{ eV}$

^a At QCISD/6-311++G(d, f) optimal geometry.

(depending on the orientation of the occupied 2p or 3p orbital) $^2\Pi_f$ or $^2\Sigma^+$ electronic states. After electron excitation of B or Al into the 4P state, stronger bonds can be expected to form with the zinc atom. We therefore studied four low-lying electronic states $^2\Pi_f$ ($1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^2 2\pi^1$), $^2\Sigma^+$ ($1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^2 2\pi^0 4\sigma^1$), $^4\Sigma^-$ ($1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^1 2\pi^2$) and $^4\Pi_f$ ($1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^1 2\pi^1 4\sigma^1$) which were derived assuming double occupancy for the 3d electrons of Zn, as well as for the lowest 2σ MO while distributing the three other valence electrons throughout the 3σ, 4σ and 2π valence orbitals. The results of our calculations are presented in tables 4 and 5.

At all levels of theory, the $^2\Pi_f$ state was found to be the ground state for BZn and AlZn. The $^2\Sigma^+$ excited state is 0.242 eV (BZn) and 0.160 eV (AlZn) higher in energy, and the two high-spin states were found to be substantially higher in energy. The calculated AlZn bond length $R_e(\text{Al-Zn}) = 2.698 \text{ \AA}$ at QCISD/6-311++G(d, f) is in excellent agreement with the experi-

mental data $R_0(\text{Al-Zn}) = 2.6957(4) \text{ \AA}$ determined by Morse and coworkers [10]. Our AlZn harmonic frequency $\omega_e = 476 \text{ cm}^{-1}$ at the QCISD/6-311++G(d, f) level of theory is substantially larger than the experimentally determined $\Delta G_{1/2} = 154.4(7) \text{ cm}^{-1}$ [10]. This unexpected failure of the QCISD/6-311++G(d, f) level of theory forced us to repeat our calculations at the QCISD(T)/6-311++G(d, f) level of theory. At this level we obtained $R_e(\text{Al-Zn}) = 2.783 \text{ \AA}$ and $\omega_e = 137 \text{ cm}^{-1}$. This last number is in fair agreement with the experimental value. Taking into account the large influence of triple excitations in frequency calculations of AlZn at the QCISD(T) method we repeated calculations of the ground electronic states of all the molecules. We found relatively modest effects from the triple excitation for all other molecules except AlZn. For example, for the valence isoelectronic BZn molecule we obtained $R_e(\text{B-Zn}) = 2.255 \text{ \AA}$ and $\omega_e = 294 \text{ cm}^{-1}$ at the QCISD(T)/6-311++G(d, f) level of theory compared with the $R_e(\text{B-Zn}) = 2.320 \text{ \AA}$ and $\omega_e = 242 \text{ cm}^{-1}$

Table 4. Calculated molecular properties of the lowest BZn states.

BZn (${}^2\Pi_r$) $1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^2 2\pi^1 4\sigma^0$	BZn (${}^2\Sigma^+$) $1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^2 2\pi^0 4\sigma^1$	BZn (${}^4\Sigma^-$) $1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^1 2\pi^2 4\sigma^0$	BZn (${}^4\Pi_r$) $1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^1 2\pi^1 4\sigma^1$
B3LYP/6-311++G(d, f) $E_{B3LYP} = -1804.029\ 605$ $R_e(\text{B-Zn}) = 2.282\ \text{\AA}$ $\omega_e = 286\ \text{cm}^{-1}$ $\langle S^2 \rangle = 0.759$ $T_{e,B3LYP} = 0.0\ \text{eV}$	B3LYP/6-311++G(d, f) $E_{B3LYP} = -1804.016\ 088$ $R_e(\text{B-Zn}) = 3.816\ \text{\AA}$ $\omega_e = 30\ \text{cm}^{-1}$ $\langle S^2 \rangle = 0.753$ $T_{e,B3LYP} = 0.368\ \text{eV}$	B3LYP/6-311++G(d, f) $E_{B3LYP} = -1803.977\ 558$ $R_e(\text{B-Zn}) = 1.942\ \text{\AA}$ $\omega_e = 581\ \text{cm}^{-1}$ $\langle S^2 \rangle = 3.762$ $T_{e,B3LYP} = 1.416\ \text{eV}$	B3LYP/6-311++G(d, f) $E_{B3LYP} = -1803.971\ 032$ $R_e(\text{B-Zn}) = 2.085\ \text{\AA}$ $\omega_e = 498\ \text{cm}^{-1}$ $\langle S^2 \rangle = 3.754$ $T_{e,B3LYP} = 1.594\ \text{eV}$
MP2/6-311++G(d, f) $E_{PMP2} = -1802.671\ 359$ $R_e(\text{B-Zn}) = 2.251\ \text{\AA}$ $\omega_e = 272\ \text{cm}^{-1}$ $\langle S^2 \rangle = 0.767$ $T_{e,PMP2} = 0.0\ \text{eV}$	MP2/6-311++G(d, f) $E_{PMP2} = -1802.663\ 833$ $R_e(\text{B-Zn}) = 4.510\ \text{\AA}$ $\omega_e = 27\ \text{cm}^{-1}$ $\langle S^2 \rangle = 0.758$ $T_{e,PMP2} = 0.205\ \text{eV}$	MP2/6-311++G(d, f) $E_{PMP2} = -1802.632\ 236$ $R_e(\text{B-Zn}) = 1.910\ \text{\AA}$ $\omega_e = 609\ \text{cm}^{-1}$ $\langle S^2 \rangle = 3.858$ $T_{e,PMP2} = 1.065\ \text{eV}$	MP2/6-311++G(d, f) $E_{PMP2} = -1802.631\ 631$ $R_e(\text{B-Zn}) = 2.056\ \text{\AA}$ $\omega_e = 536\ \text{cm}^{-1}$ $\langle S^2 \rangle = 3.759$ $T_{e,PMP2} = 1.081\ \text{eV}$
QCISD/6-311++G(d, f) $E_{QCISD} = -1802.660\ 557$ $R_e(\text{B-Zn}) = 2.320\ \text{\AA}$ $\omega_e = 242\ \text{cm}^{-1}$ $\langle S^2 \rangle = 0.770$ $T_{e,QCISD} = 0.0\ \text{eV}$ $Q^{\text{Mull}}(\text{B}) = -0.075\ e$ $Q^{\text{NPA}}(\text{B}) = -0.313\ e$ $Q^{\text{Spin}}(\text{B}) = 0.944\ e$ $\mu_e = 1.439\ \text{D}$	QCISD/6-311++G(d, f) $E_{QCISD} = -1802.655\ 557$ $R_e(\text{B-Zn}) = 4.548\ \text{\AA}$ $\omega_e = 23\ \text{cm}^{-1}$ $\langle S^2 \rangle = 0.758$ $T_{e,QCISD} = 0.136\ \text{eV}$ $Q^{\text{Mull}}(\text{B}) = +0.007\ e$ $Q^{\text{NPA}}(\text{B}) = +0.000\ e$ $Q^{\text{Spin}}(\text{B}) = 0.992\ e$ $\mu_e = 0.171\ \text{D}$	QCISD/6-311++G(d, f) $E_{QCISD} = -1802.614\ 633$ $R_e(\text{B-Zn}) = 1.957\ \text{\AA}$ $\omega_e = 580\ \text{cm}^{-1}$ $\langle S^2 \rangle = 3.865$ $T_{e,QCISD} = 1.250\ \text{eV}$ $Q^{\text{Mull}}(\text{B}) = -0.258\ e$ $Q^{\text{NPA}}(\text{B}) = -0.773\ e$ $Q^{\text{Spin}}(\text{B}) = 2.093\ e$ $\mu_e = 3.015\ \text{D}$	QCISD/6-311++G(d, f) $E_{QCISD} = -1802.612\ 035$ $R_e(\text{B-Zn}) = 2.086\ \text{\AA}$ $\omega_e = 513\ \text{cm}^{-1}$ $\langle S^2 \rangle = 3.759$ $T_{e,QCISD} = 1.320\ \text{eV}$ $Q^{\text{Mull}}(\text{B}) = -0.181\ e$ $Q^{\text{NPA}}(\text{B}) = -0.658\ e$ $Q^{\text{Spin}}(\text{B}) = 0.449\ e$ $\mu_e = 0.804\ \text{D}$
QCISD/6-311++G(2d, 2f) $E_{QCISD(T)} = -1802.744\ 785$ $R(\text{B-Zn}) = 2.320\ \text{\AA}^a$ $T_{e,QCISD(T)} = 0.0\ \text{eV}$	QCISD/6-311++G(2d, 2f) $E_{QCISD(T)} = -1802.735\ 875$ $R(\text{B-Zn}) = 4.548\ \text{\AA}^a$ $T_{e,QCISD(T)} = 0.242\ \text{eV}$	QCISD/6-311++G(2d, 2f) $E_{QCISD(T)} = -1802.696\ 145$ $R(\text{B-Zn}) = 1.957\ \text{\AA}^a$ $T_{e,QCISD(T)} = 1.323\ \text{eV}$	QCISD/6-311++G(2d, 2f) $E_{QCISD(T)} = -1802.690\ 326$ $R(\text{B-Zn}) = 2.086\ \text{\AA}^a$ $T_{e,QCISD(T)} = 1.482\ \text{eV}$

^a At QCISD/6-311++G(d, f) optimal geometry.

at the QCISD/6-311++G(d, f) level of theory. We will discuss in more detail the influence of triple excitations in the QCISD(T) method on the molecular properties in a future article. For BZn and AlZn, the calculated dissociation energies were found to be 0.252 eV and 0.177 eV, respectively. The charge transfers from Zn to B (0.31 e) and to Al (0.20 e) in the ground states of BZn and AlZn are substantially larger than in the ground states of LiZn, NaZn, BeZn and MgZn, in spite of the relatively small atomic electron affinities of B (0.277 (10) eV [1]) and of Al (0.441 (10) eV [1]). These charge separations result in relatively large dipole moments of 1.44 D (BZn) and 0.73 D (AlZn) for such weakly bound molecules, which may render these molecules accessible to microwave spectroscopy.

Both high spin states of BZn and AlZn have substantially shorter bond lengths than the ground state, which suggests that these states have chemical bonding rather than van der Waals bonds. Indeed, our calculated intrinsic bond energies for the two lowest excited quartet

states were found to be relatively high: 2.46 eV (${}^4\Sigma^-$, BZn); 2.30 eV (${}^4\Pi_r$, BZn); 1.72 eV (${}^4\Sigma^-$, AlZn) and 1.50 eV (${}^4\Pi_r$, AlZn). However, these intrinsic bond energies are not able to overcome the excitation energies of B (3.53 eV at QCISD(T)/6-311++G(2d, 2f), 3.57 eV experiment [2]) or of Al (3.40 eV at QCISD(T)/6-311++G(2d, 2f), 3.61 eV experiment [2]), as a result of which the doublet ${}^2\Pi_r$ state with its weak van der Waals bond remains the ground state.

3.4. CZn and SiZn

There are no experimental or theoretical data on these molecules in the literature according to *Spectroscopic References for Diatomic Molecules* [4]

Carbon and silicon atoms have $2s^2 2p^2$ (C) and $3s^2 3p^2$ (Si) valence electronic configurations, so without electronic excitation one expects only a weak van der Waals bond or a dative bond with the zinc atom producing (depending on the orientation of the 2p

Table 5. Calculated molecular properties of the lowest AlZn states.

AlZn (${}^2\Pi_r$) $1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^2 2\pi^1 4\sigma^0$	AlZn (${}^2\Sigma^+$) $1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^2 2\pi^0 4\sigma^1$	AlZn (${}^4\Sigma^-$) $1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^1 2\pi^2 4\sigma^0$	AlZn (${}^4\Pi_r$) $1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^1 2\pi^1 4\sigma^1$
B3LYP/6-311++G(d, f) $E_{B3LYP} = -2021.748\,910$ $R_e(\text{Al-Zn}) = 2.768\text{ \AA}$ $\omega_e = 144\text{ cm}^{-1}$ $\langle S^2 \rangle = 0.753$ $T_{e,B3LYP} = 0.0\text{ eV}$	B3LYP/6-311++G(d, f) $E_{B3LYP} = -2021.741\,898$ $R_e(\text{Al-Zn}) = 3.432\text{ \AA}$ $\omega_e = 49\text{ cm}^{-1}$ $\langle S^2 \rangle = 0.757$ $T_{e,B3LYP} = 0.191\text{ eV}$	B3LYP/6-311++G(d, f) $E_{B3LYP} = -2021.670\,561$ $R_e(\text{Al-Zn}) = 2.332\text{ \AA}$ $\omega_e = 321\text{ cm}^{-1}$ $\langle S^2 \rangle = 3.757$ $T_{e,B3LYP} = 2.132\text{ eV}$	B3LYP/6-311++G(d, f) $E_{B3LYP} = -2021.663\,696$ $R_e(\text{Al-Zn}) = 2.525\text{ \AA}$ $\omega_e = 262\text{ cm}^{-1}$ $\langle S^2 \rangle = 3.752$ $T_{e,B3LYP} = 2.319\text{ eV}$
MP2/6-311++G(d, f) $E_{PMP2} = -2020.002\,819$ $R_e(\text{Al-Zn}) = 2.630\text{ \AA}$ $\omega_e = 278\text{ cm}^{-1}$ $\langle S^2 \rangle = 0.781$ $T_{e,PMP2} = 0.0\text{ eV}$	MP2/6-311++G(d, f) $E_{PMP2} = -2019.996\,990$ $R_e(\text{Al-Zn}) = 4.556\text{ \AA}$ $\omega_e = 23\text{ cm}^{-1}$ $\langle S^2 \rangle = 0.764$ $T_{e,PMP2} = 0.159\text{ eV}$	MP2/6-311++G(d, f) $E_{PMP2} = -2019.941\,279$ $R_e(\text{Al-Zn}) = 2.286\text{ \AA}$ $\omega_e = 356\text{ cm}^{-1}$ $\langle S^2 \rangle = 3.836$ $T_{e,PMP2} = 1.675\text{ eV}$	MP2/6-311++G(d, f) $E_{PMP2} = -2019.935\,428$ $R_e(\text{Al-Zn}) = 2.476\text{ \AA}$ $\omega_e = 294\text{ cm}^{-1}$ $\langle S^2 \rangle = 3.756$ $T_{e,PMP2} = 1.834\text{ eV}$
QCISD/6-311++G(d, f) $E_{QCISD} = -2019.985\,577$ $R_e(\text{Al-Zn}) = 2.698\text{ \AA}$ $\omega_e = 476\text{ cm}^{-1}$ $\langle S^2 \rangle = 0.812$ $T_{e,QCISD} = 0.0\text{ eV}$ $Q^{\text{Mull}}(\text{Al}) = +0.067\text{ e}$ $Q^{\text{NPA}}(\text{Al}) = -0.202\text{ e}$ $Q^{\text{Spin}}(\text{Al}) = 0.697\text{ e}$ $\mu_e = 0.731\text{ D}$	QCISD/6-311++G(d, f) $E_{QCISD} = -2019.981\,832$ $R_e(\text{Al-Zn}) = 3.915\text{ \AA}$ $\omega_e = 16\text{ cm}^{-1}$ $\langle S^2 \rangle = 0.787$ $T_{e,QCISD} = 0.102\text{ eV}$ $Q^{\text{Mull}}(\text{Al}) = +0.070\text{ e}$ $Q^{\text{NPA}}(\text{Al}) = +0.010\text{ e}$ $Q^{\text{Spin}}(\text{Al}) = 0.904\text{ e}$ $\mu_e = 0.899\text{ D}$	QCISD/6-311++G(d, f) $E_{QCISD} = -2019.919\,776$ $R_e(\text{Al-Zn}) = 2.344\text{ \AA}$ $\omega_e = 323\text{ cm}^{-1}$ $\langle S^2 \rangle = 3.845$ $T_{e,QCISD} = 1.790\text{ eV}$ $Q^{\text{Mull}}(\text{Al}) = -0.018\text{ e}$ $Q^{\text{NPA}}(\text{Al}) = -0.531\text{ e}$ $Q^{\text{Spin}}(\text{Al}) = 2.033\text{ e}$ $\mu_e = 1.409\text{ D}$	QCISD/6-311++G(d, f) $E_{QCISD} = -2019.914\,186$ $R_e(\text{Al-Zn}) = 2.514\text{ \AA}$ $\omega_e = 278\text{ cm}^{-1}$ $\langle S^2 \rangle = 3.756$ $T_{e,QCISD} = 1.943\text{ eV}$ $Q^{\text{Mull}}(\text{Al}) = +0.040\text{ e}$ $Q^{\text{NPA}}(\text{Al}) = -0.482\text{ e}$ $Q^{\text{Spin}}(\text{Al}) = 1.693\text{ e}$ $\mu_e = 0.292\text{ D}$
QCISD(T)/6-311++G(2d, 2f) $E_{QCISD(T)} = -2020.070\,946$ $R(\text{Al-Zn}) = 2.698\text{ \AA}^a$ $T_{e,QCISD(T)} = 0.0\text{ eV}$	QCISD(T)/6-311++G(2d, 2f) $E_{QCISD(T)} = -2020.065\,074$ $R(\text{Al-Zn}) = 3.915\text{ \AA}^a$ $T_{e,QCISD(T)} = 0.160\text{ eV}$	QCISD(T)/6-311++G(2d, 2f) $E_{QCISD(T)} = -2020.002\,790$ $R(\text{Al-Zn}) = 2.344\text{ \AA}^a$ $T_{e,QCISD(T)} = 1.855\text{ eV}$	QCISD(T)/6-311++G(2d, 2f) $E_{QCISD(T)} = -2019.994\,633$ $R(\text{Al-Zn}) = 2.514\text{ \AA}^a$ $T_{e,QCISD(T)} = 2.076\text{ eV}$

^a At QCISD/6-311++G(d, f) optimal geometry.

or 3p orbital hole) ${}^3\Pi_r$ or ${}^3\Sigma^-$ electronic states. After electron excitation into the 5S state, stronger bonds can be expected for form with the zinc atom. Therefore, we studied four low lying electronic states, ${}^3\Sigma^-$ ($1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^2 2\pi^2$), ${}^3\Pi_r$ ($1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^2 2\pi^1 4\sigma^1$), ${}^3\Pi_i$ ($1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^1 2\pi^3$) and ${}^5\Sigma^-$ ($1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^1 2\pi^2 4\sigma^1$), which were derived assuming double occupancy for the 3d electrons of Zn, and for the lowest 2σ MO while distributing the four other valence electrons throughout the 3σ, 4σ and 2π valence orbitals. The results of our calculations are presented in tables 6 and 7.

At all levels of theory, the ${}^3\Sigma^-$ state was found to be the ground state for CZn and SiZn. The ${}^3\Pi_r$ excited state is 0.916 eV (CZn) and 0.577 eV (SiZn) higher in energy, and the two other states were found to be substantially higher in energy. The calculated ${}^3\Sigma^-$ bond lengths: $R_e(\text{C-Zn}) = 1.992\text{ \AA}$ and $R_e(\text{Si-Zn}) = 2.451\text{ \AA}$ at QCISD/6-311++G(d, f) are surprisingly short, which suggests that the bonding between C or

Si and Zn is chemical rather than van der Waals. Our CZn and SiZn harmonic frequencies $\omega_e(\text{CZn}) = 482\text{ cm}^{-1}$ and $\omega_e(\text{SiZn}) = 231\text{ cm}^{-1}$ support this picture, as do our calculated dissociation energies 0.923 eV (CZn) and 0.591 eV (SiZn). The reason for the relatively strong bonds for CZn and SiZn is probably the high electron affinities of C (1.2629(3) eV [1]) and Si (1.385(5) eV [1]), which makes possible a relatively large charge transfer from Zn to C or Si. Our calculated charge transfer to C (0.66 e) and to Si (0.43 e) supports this picture of the bonding. These charge separations result in large dipole moments of 2.77 D (CZn) and 2.12 D (SiZn), which may render these molecules accessible to microwave spectroscopy.

The lowest ${}^3\Pi_r$ excited states of CZn and SiZn are substantially less bound with long bond lengths $R_e(\text{C-Zn}) = 4.489\text{ \AA}$ and $R_e(\text{Si-Zn}) = 4.399\text{ \AA}$ and weak bond energies: $D_e(\text{C-Zn}) = 0.008\text{ eV}$ and $D_e(\text{Si-Zn}) = 0.014\text{ eV}$, and therefore CZn and SiZn in the ${}^3\Pi_r$ state have van der Waals bonding.

Table 6. Calculated molecular properties of the lowest CZn states.

CZn ($^3\Sigma^-$) $1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^2 2\pi^2 4\sigma^0$	CZn ($^3\Pi_f$) $1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^2 2\pi^1 4\sigma^1$	CZn ($^5\Sigma^-$) $1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^1 2\pi^2 4\sigma^1$	CZn ($^3\Pi_i$) $1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^1 2\pi^3 4\sigma^0$
B3LYP/6-311++G(d, f) $E_{B3LYP} = -1817.247\ 634$ $R_e(\text{C-Zn}) = 2.011\ \text{\AA}$ $\omega_e = 440\ \text{cm}^{-1}$ $\langle S^2 \rangle = 2.120$ $T_{e,B3LYP} = 0.0\ \text{eV}$	B3LYP/6-311++G(d, f) $E_{B3LYP} = -1817.213\ 789$ $R_e(\text{C-Zn}) = 2.317\ \text{\AA}$ $\omega_e = 194\ \text{cm}^{-1}$ $\langle S^2 \rangle = 2.014$ $T_{e,B3LYP} = 0.921\ \text{eV}$	B3LYP/6-311++G(d, f) $E_{B3LYP} = -1817.198\ 364$ $R_e(\text{C-Zn}) = 1.950\ \text{\AA}$ $\omega_e = 556\ \text{cm}^{-1}$ $\langle S^2 \rangle = 6.004$ $T_{e,B3LYP} = 1.341\ \text{eV}$	B3LYP/6-311++G(d, f) $E_{B3LYP} = -1817.144\ 251$ $R_e(\text{C-Zn}) = 1.808\ \text{\AA}$ $\omega_e = 687\ \text{cm}^{-1}$ $\langle S^2 \rangle = 2.016$ $T_{e,B3LYP} = 2.813\ \text{eV}$
MP2/6-311++G(d, f) $E_{PMP2} = -1815.871\ 666$ $R_e(\text{C-Zn}) = 1.970\ \text{\AA}$ $\omega_e = 513\ \text{cm}^{-1}$ $\langle S^2 \rangle = 2.827$ $T_{e,PMP2} = 0.0\ \text{eV}$	MP2/6-311++G(d, f) $E_{PMP2} = -1815.839\ 828$ $R_e(\text{C-Zn}) = 4.391\ \text{\AA}$ $\omega_e = 22\ \text{cm}^{-1}$ $\langle S^2 \rangle = 2.008$ $T_{e,PMP2} = 0.866\ \text{eV}$	MP2/6-311++G(d, f) $E_{PMP2} = -1815.846\ 983$ $R_e(\text{C-Zn}) = 1.922\ \text{\AA}$ $\omega_e = 604\ \text{cm}^{-1}$ $\langle S^2 \rangle = 6.010$ $T_{e,PMP2} = 0.672\ \text{eV}$	MP2/6-311++G(d, f) $E_{PMP2} = -1815.757\ 473$ $R_e(\text{C-Zn}) = 1.755\ \text{\AA}$ $\omega_e = 726\ \text{cm}^{-1}$ $\langle S^2 \rangle = 2.594$ $T_{e,PMP2} = 3.107\ \text{eV}$
QCISD/6-311++G(d, f) $E_{QCISD} = -1815.857\ 733$ $R_e(\text{C-Zn}) = 1.992\ \text{\AA}$ $\omega_e = 482\ \text{cm}^{-1}$ $\langle S^2 \rangle = 2.823$ $T_{e,QCISD} = 0.0\ \text{eV}$ $Q^{\text{Mull}}(\text{C}) = -0.236\ e$ $Q^{\text{NPA}}(\text{C}) = -0.657\ e$ $Q^{\text{Spin}}(\text{C}) = 2.318\ e$ $\mu_e = 2.771\ \text{D}$	QCISD/6-311++G(d, f) $E_{QCISD} = -1815.830\ 699$ $R_e(\text{C-Zn}) = 4.489\ \text{\AA}$ $\omega_e = 20\ \text{cm}^{-1}$ $\langle S^2 \rangle = 2.008$ $T_{e,QCISD} = 0.736\ \text{eV}$ $Q^{\text{Mull}}(\text{C}) = +0.005\ e$ $Q^{\text{NPA}}(\text{C}) = -0.000\ e$ $Q^{\text{Spin}}(\text{C}) = 1.997\ e$ $\mu_e = 0.065\ \text{D}$	QCISD/6-311++G(d, f) $E_{QCISD} = -1815.827\ 970$ $R_e(\text{C-Zn}) = 1.942\ \text{\AA}$ $\omega_e = 587\ \text{cm}^{-1}$ $\langle S^2 \rangle = 6.010$ $T_{e,QCISD} = 0.810\ \text{eV}$ $Q^{\text{Mull}}(\text{C}) = -0.312\ e$ $Q^{\text{NPA}}(\text{C}) = -0.785\ e$ $Q^{\text{Spin}}(\text{C}) = 2.762\ e$ $\mu_e = 1.749\ \text{D}$	QCISD/6-311++G(d, f) $E_{QCISD} = -1815.757\ 037$ $R_e(\text{C-Zn}) = 1.821\ \text{\AA}$ $\omega_e = 712\ \text{cm}^{-1}$ $\langle S^2 \rangle = 2.080$ $T_{e,QCISD} = 2.740\ \text{eV}$ $Q^{\text{Mull}}(\text{C}) = -0.337\ e$ $Q^{\text{NPA}}(\text{C}) = -1.047\ e$ $Q^{\text{Spin}}(\text{C}) = 1.452\ e$ $\mu_e = 4.184\ \text{D}$
QCISD(T)/6-311++G(2d, 2f) $E_{QCISD(T)} = -1815.948\ 395$ $R(\text{C-Zn}) = 1.992\ \text{\AA}^a$ $T_{e,QCISD(T)} = 0.0\ \text{eV}$	QCISD(T)/6-311++G(2d, 2f) $E_{QCISD(T)} = -1815.914\ 730$ $R(\text{C-Zn}) = 4.489\ \text{\AA}^a$ $T_{e,QCISD(T)} = 0.916\ \text{eV}$	QCISD(T)/6-311++G(2d, 2f) $E_{QCISD(T)} = -1815.910\ 256$ $R(\text{C-Zn}) = 1.942\ \text{\AA}^a$ $T_{e,QCISD(T)} = 1.038\ \text{eV}$	QCISD(T)/6-311++G(2d, 2f) $E_{QCISD(T)} = -1815.846\ 905$ $R(\text{C-Zn}) = 1.821\ \text{\AA}^a$ $T_{e,QCISD(T)} = 2.762\ \text{eV}$

^a At QCISD/6-311++G(d, f) optimal geometry.

The high-spin $^5\Sigma^-$ states of CZn and SiZn have bond lengths similar to those in ground state, which suggests that these states have chemical bonding rather than van der Waals bonds. Indeed, our calculated intrinsic bond energies for the two lowest excited quartet states were found to be relatively high: 3.70 eV (dissociation into $^3\text{P}(\text{C}) + ^3\text{P}(\text{Zn})$) and 2.68 eV (dissociation into $^5\text{S}(\text{Si}) + ^1\text{S}(\text{Zn})$). However, these intrinsic bond energies are not able to overcome the excitation energies of C (^5S ; 4.01 eV at QCISD(T)/6-311++G(2d, 2f), 4.18 eV experiment [2]), Zn (^3P ; 3.82 eV at QCISD(T)/6-311++G(2d, 2f), 4.04 eV experiment [2]) or of Si (^5S ; 3.79 eV at QCISD(T)/6-311++G(2d, 2f)) while they are very close, as a result of which the triplet $^3\Sigma^-$ state remains the ground state.

3.5. NZn and PZn

There are no experimental or theoretical data on these molecules in the literature according to *Spectroscopic References for Diatomic Molecules* [4]

Nitrogen and phosphorus have very stable ^4S ($2s^2 2p^3$ (N) and $3s^2 3p^3$ (P)) electronic configurations, and nitrogen does not have a positive electron affinity while phosphorus has an electron affinity of 0.7465(3) eV [1]. Therefore, one expects only a weak van der Waals bond with the zinc atom in the $^4\Sigma^-$ electronic states. After electron excitation into the ^2D state, stronger bonds can be expected to form with the zinc atom. We therefore studied two low lying electronic states, $^4\Sigma^-$ ($1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^2 2\pi^2 4\sigma^1$) and $^2\Pi_i$ ($1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^2 2\pi^3 4\sigma^0$). The results of our calculations are presented in table 8.

At all levels of theory, the $^4\Sigma^-$ state was found to be the ground state for NZn and PZn. Interestingly, for this state we found *two minima* for both molecules at the MP2/6-311++G(d, f) level of theory. In the short bond minimum (NZn: $R_e(\text{N-Zn}) = 2.028\ \text{\AA}$, $\omega_e = 321\ \text{cm}^{-1}$ and PZn: $R_e(\text{P-Zn}) = 2.449\ \text{\AA}$, $\omega_e = 189\ \text{cm}^{-1}$) the bonding is chemical. Although the 2π MO is almost completely composed of 3p AOs of P,

Table 7. Calculated molecular properties of the lowest SiZn states.

SiZn ($^3\Sigma^-$) $1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^2 2\pi^2 4\sigma^0$	SiZn ($^3\Pi_f$) $1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^2 2\pi^1 4\sigma^1$	SiZn ($^5\Sigma^-$) $1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^1 2\pi^2 4\sigma^1$	SiZn ($^3\Pi_g$) $1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^1 2\pi^3 4\sigma^0$
B3LYP/6-311++G(d, f) $E_{B3LYP} = -2068.773\ 207$ $R_e(\text{Si-Zn}) = 2.436\ \text{\AA}$ $\omega_e = 236\ \text{cm}^{-1}$ $\langle S^2 \rangle = 2.011$ $T_{e,B3LYP} = 0.0\ \text{eV}$	B3LYP/6-311++G(d, f) $E_{B3LYP} = -2068.751\ 541$ $R_e(\text{Si-Zn}) = 2.818\ \text{\AA}$ $\omega_e = 117\ \text{cm}^{-1}$ $\langle S^2 \rangle = 2.009$ $T_{e,B3LYP} = 0.590\ \text{eV}$	B3LYP/6-311++G(d, f) $E_{B3LYP} = -2068.696\ 049$ $R_e(\text{Si-Zn}) = 2.385\ \text{\AA}$ $\omega_e = 297\ \text{cm}^{-1}$ $\langle S^2 \rangle = 6.004$ $T_{e,B3LYP} = 2.099\ \text{eV}$	B3LYP/6-311++G(d, f) $E_{B3LYP} = -2068.660\ 399$ $R_e(\text{Si-Zn}) = 2.197\ \text{\AA}$ $\omega_e = 375\ \text{cm}^{-1}$ $\langle S^2 \rangle = 2.008$ $T_{e,B3LYP} = 3.069\ \text{eV}$
MP2/6-311++G(d, f) $E_{PMP2} = -2067.006\ 516$ $R_e(\text{Si-Zn}) = 2.437\ \text{\AA}$ $\omega_e = 232\ \text{cm}^{-1}$ $\langle S^2 \rangle = 2.532$ $T_{e,PMP2} = 0.0\ \text{eV}$	MP2/6-311++G(d, f) $E_{PMP2} = -2066.986\ 697$ $R_e(\text{Si-Zn}) = 2.818\ \text{\AA}$ $\omega_e = 58\ \text{cm}^{-1}$ $\langle S^2 \rangle = 2.072$ $T_{e,PMP2} = 0.539\ \text{eV}$	MP2/6-311++G(d, f) $E_{PMP2} = -2066.955\ 629$ $R_e(\text{Si-Zn}) = 2.338\ \text{\AA}$ $\omega_e = 330\ \text{cm}^{-1}$ $\langle S^2 \rangle = 6.004$ $T_{e,PMP2} = 1.385\ \text{eV}$	MP2/6-311++G(d, f) $E_{PMP2} = -2066.901\ 533$ $R_e(\text{Si-Zn}) = 2.147\ \text{\AA}$ $\omega_e = 432\ \text{cm}^{-1}$ $\langle S^2 \rangle = 2.087$ $T_{e,PMP2} = 2.857\ \text{eV}$
QCISD/6-311++G(d, f) $E_{QCISD} = -2066.991\ 781$ $R_e(\text{Si-Zn}) = 2.451\ \text{\AA}$ $\omega_e = 231\ \text{cm}^{-1}$ $\langle S^2 \rangle = 2.529$ $T_{e,QCISD} = 0.0\ \text{eV}$ $Q^{\text{Mull}}(\text{Si}) = -0.047\ e$ $Q^{\text{NPA}}(\text{Si}) = -0.434\ e$ $Q^{\text{Spin}}(\text{Si}) = 1.711\ e$ $\mu_e = 2.121\ \text{D}$	QCISD/6-311++G(d, f) $E_{QCISD} = -2066.973\ 138$ $R_e(\text{Si-Zn}) = 4.399\ \text{\AA}$ $\omega_e = 19\ \text{cm}^{-1}$ $\langle S^2 \rangle = 2.009$ $T_{e,QCISD} = 0.507\ \text{eV}$ $Q^{\text{Mull}}(\text{Si}) = +0.012\ e$ $Q^{\text{NPA}}(\text{Si}) = -0.001\ e$ $Q^{\text{Spin}}(\text{Si}) = 1.985\ e$ $\mu_e = 0.173\ \text{D}$	QCISD/6-311++G(d, f) $E_{QCISD} = -2066.936\ 073$ $R_e(\text{Si-Zn}) = 2.364\ \text{\AA}$ $\omega_e = 321\ \text{cm}^{-1}$ $\langle S^2 \rangle = 6.004$ $T_{e,QCISD} = 1.516\ \text{eV}$ $Q^{\text{Mull}}(\text{Si}) = -0.119\ e$ $Q^{\text{NPA}}(\text{Si}) = -0.653\ e$ $Q^{\text{Spin}}(\text{Si}) = 2.610\ e$ $\mu_e = 0.966\ \text{D}$	QCISD/6-311++G(d, f) ^b $E_{QCISD} = -2066.936\ 073$ $R_e(\text{Si-Zn}) = 2.364\ \text{\AA}$ $\omega_e = 321\ \text{cm}^{-1}$ $\langle S^2 \rangle = 6.004$ $T_{e,QCISD} = 1.516\ \text{eV}$ $Q^{\text{Mull}}(\text{Si}) = -0.119\ e$ $Q^{\text{NPA}}(\text{Si}) = -0.653\ e$ $Q^{\text{Spin}}(\text{Si}) = 2.610\ e$ $\mu_e = 0.966\ \text{D}$
QCISD/6-311++G(2d, 2f) $E_{QCISD} = -2067.084\ 256$ $R(\text{Si-Zn}) = 2.451\ \text{\AA}^a$ $T_{e,QCISD} = 0.0\ \text{eV}$	QCISD/6-311++G(2d, 2f) $E_{QCISD} = -2067.063\ 055$ $R(\text{Si-Zn}) = 4.399\ \text{\AA}^a$ $T_{e,QCISD} = 0.577\ \text{eV}$	QCISD/6-311++G(2d, 2f) $E_{QCISD} = -2067.021\ 741$ $R(\text{Si-Zn}) = 2.364\ \text{\AA}^a$ $T_{e,QCISD} = 1.701\ \text{eV}$	

^a At QCISD/6-311++G(d, f) optimal geometry.

^b There is a sharp change in the composition of the wavefunction at the QCISD level of theory around the equilibrium bond length.

the 3σ and 4σ MOs are composed from AOs of both atoms; the 3σ MO is singly occupied and it is a bonding orbital composed of $4s$ AOs of Zn and $3p$ AOs of P, and the 4σ MO is doubly occupied (even being higher in energy than the 3σ MO) and is antibonding with respect to overlap of the $3p$ AOs of P and the $4s$ AOs of Zn, but it is bonding with respect to overlap of the $3p$ AOs of P and the $4p$ AO of Zn. The long bond minimum (NZn: $R_e(\text{N-Zn}) = 4.263\ \text{\AA}$, $\omega_e = 20\ \text{cm}^{-1}$ and PZn: $R_e(\text{P-Zn}) = 4.321\ \text{\AA}$, $\omega_e = 23\ \text{cm}^{-1}$) represents van der Waals bonding with the 2π MO completely composed of $3p$ AOs of P, the 3σ MO singly occupied and composed of the $3p$ AOs of P and the 4σ MO doubly occupied (even being higher in energy than the 3σ MO) and composed of the $4s$ AO of Zn.

The short minima were found to be higher (by $0.097\ \text{eV}$) and lower (by $0.055\ \text{eV}$) in energy than the long minima at the MP2/6-311++G(d, f) level of theory for NZn and PZn, respectively. However, at the B3LYP/6-311++G(d, f) level of theory, only the short

minima were found for both molecules. At the QCISD/6-311++G(d, f) level of theory, only PZn has two minima, while the short minimum of NZn does not exist. Further studies must be done for NZn to make a final conclusion on the short minimum. At our highest QCISD(T)/6-311++G(2d, 2f) level the short minimum of PZn is somewhat (by $0.018\ \text{eV}$) lower in energy than the long one, but it is hard to predict which minimum is more stable at this time.

The $^2\Pi_i$ excited state is $0.738\ \text{eV}$ (NZn) and $0.502\ \text{eV}$ (PZn) higher in energy. In the $^2\Pi_i$ excited state, the charge transfer from Zn to N or to P is substantial, which is reflected in the chemical bonding in this state. Indeed, the calculated molecular parameters of the $^2\Pi_i$ state $R_e(\text{N-Zn}) = 1.84\ \text{\AA}$ and $R_e(\text{P-Zn}) = 2.21\ \text{\AA}$, $\omega_e = 602\ \text{cm}^{-1}$ (NZn) and $\omega_e = 354\ \text{cm}^{-1}$ (PZn), and strong intrinsic bond energies $1.65\ \text{eV}$ (NZn) and $0.94\ \text{eV}$ (PZn) support the chemical nature of the bonding. However, these intrinsic bond energies are not able to overcome the excitation energies of N (^2D ;

Table 8. Calculated molecular properties of the lowest NZn and PZn states.

NZn ($4\Sigma^-$) ^b $1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^2 2\pi^2 4\sigma^1$	NZn ($^2\Pi_i$) $1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^2 2\pi^3 4\sigma^0$	PZn ($4\Sigma^-$) ^a $1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^2 2\pi^2 4\sigma^1$	PZn ($^4\Sigma^-$) ^b $1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^2 2\pi^2 4\sigma^1$	PZn ($^2\Pi_i$) $1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^2 2\pi^3 4\sigma^0$
B3LYP/6-311++G(d, f) No long-bond minimum	B3LYP/6-311++G(d, f) $E_{\text{B3LYP}} = -1833.937764$ $R_e(\text{N-Zn}) = 1.839 \text{ \AA}$ $\omega_e = 580 \text{ cm}^{-1}$ $\langle S^2 \rangle = 0.951$	B3LYP/6-311++G(d, f) $E_{\text{B3LYP}} = -2120.646308$ $R_e(\text{P-Zn}) = 2.511 \text{ \AA}$ $\omega_e = 189 \text{ cm}^{-1}$ $\langle S^2 \rangle = 3.759$ $T_{e,\text{B3LYP}} = 0.0 \text{ eV}$	B3LYP/6-311++G(d, f) No long-bond minimum	B3LYP/6-311++G(d, f) $E_{\text{B3LYP}} = -2120.633861$ $R_e(\text{P-Zn}) = 2.219 \text{ \AA}$ $\omega_e = 347 \text{ cm}^{-1}$ $\langle S^2 \rangle = 0.760$ $T_{e,\text{B3LYP}} = 0.339 \text{ eV}$
MP2/6-311++G(d, f) $E_{\text{MP2}} = -1832.570117$ $R_e(\text{N-Zn}) = 4.263 \text{ \AA}$ $\omega_e = 20 \text{ cm}^{-1}$ $\langle S^2 \rangle = 3.758$ $T_{e,\text{MP2}} = 0.0 \text{ eV}$	MP2/6-311++G(d, f) $E_{\text{MP2}} = -1832.536252$ $R_e(\text{N-Zn}) = 1.761 \text{ \AA}$ $\omega_e = 770 \text{ cm}^{-1}$ $\langle S^2 \rangle = 0.770$ $T_{e,\text{MP2}} = 0.922 \text{ eV}$	MP2/6-311++G(d, f) $E_{\text{MP2}} = -2118.864098$ $R_e(\text{P-Zn}) = 2.449 \text{ \AA}$ $\omega_e = 189 \text{ cm}^{-1}$ $\langle S^2 \rangle = 3.791$ $T_{e,\text{MP2}} = 0.0 \text{ eV}$	MP2/6-311++G(d, f) $E_{\text{MP2}} = -2118.862086$ $R_e(\text{P-Zn}) = 4.321 \text{ \AA}$ $\omega_e = 23 \text{ cm}^{-1}$ $\langle S^2 \rangle = 3.752$ $T_{e,\text{MP2}} = 0.055 \text{ eV}$	MP2/6-311++G(d, f) $E_{\text{MP2}} = -2118.844084$ $R_e(\text{P-Zn}) = 2.178 \text{ \AA}$ $\omega_e = 392 \text{ cm}^{-1}$ $\langle S^2 \rangle = 0.770$ $T_{e,\text{MP2}} = 0.545 \text{ eV}$
QCISD/6-311++G(d, f) $E_{\text{QCISD}} = -1832.556399$ $R_e(\text{N-Zn}) = 4.380 \text{ \AA}$ $\omega_e = 18 \text{ cm}^{-1}$ $\langle S^2 \rangle = 3.758$ $T_{e,\text{QCISD}} = 0.0 \text{ eV}$	QCISD/6-311++G(d, f) $E_{\text{QCISD}} = -1832.516248$ $R_e(\text{N-Zn}) = 1.841 \text{ \AA}$ $\omega_e = 602 \text{ cm}^{-1}$ $\langle S^2 \rangle = 0.768$ $T_{e,\text{QCISD}} = 1.093 \text{ eV}$	QCISD/6-311++G(d, f) $E_{\text{QCISD}} = -2118.849123$ $R_e(\text{P-Zn}) = 2.549 \text{ \AA}$ $\omega_e = 134 \text{ cm}^{-1}$ $\langle S^2 \rangle = 3.806$ $T_{e,\text{QCISD}} = 0.0 \text{ eV}$	QCISD/6-311++G(d, f) $E_{\text{QCISD}} = -2118.849204$ $R_e(\text{P-Zn}) = 4.371 \text{ \AA}$ $\omega_e = 19 \text{ cm}^{-1}$ $\langle S^2 \rangle = 3.752$ $T_{e,\text{QCISD}} = -0.002 \text{ eV}$	QCISD/6-311++G(d, f) $E_{\text{QCISD}} = -2118.826155$ $R_e(\text{P-Zn}) = 2.213 \text{ \AA}$ $\omega_e = 354 \text{ cm}^{-1}$ $\langle S^2 \rangle = 0.777$ $T_{e,\text{QCISD}} = 0.625 \text{ eV}$
$Q_{\text{Multi}}(\text{N}) = +0.003 e$ $Q_{\text{NPA}}(\text{N}) = -0.000 e$ $Q_{\text{Spin}}(\text{N}) = 2.998 e$ $\mu_e = 0.016 \text{ D}$	$Q_{\text{Multi}}(\text{N}) = -0.242 e$ $Q_{\text{NPA}}(\text{N}) = -0.882 e$ $Q_{\text{Spin}}(\text{N}) = 1.241 e$ $\mu_e = 4.059 \text{ D}$	$Q_{\text{Multi}}(\text{P}) = +0.075 e$ $Q_{\text{NPA}}(\text{P}) = -0.262 e$ $Q_{\text{Spin}}(\text{P}) = 2.564 e$ $\mu_e = 0.336 \text{ D}$	$Q_{\text{Multi}}(\text{P}) = +0.010 e$ $Q_{\text{NPA}}(\text{P}) = -0.002 e$ $Q_{\text{Spin}}(\text{P}) = 2.994 e$ $\mu_e = 0.021 \text{ D}$	$Q_{\text{Multi}}(\text{P}) = -0.145 e$ $Q_{\text{NPA}}(\text{P}) = -0.685 e$ $Q_{\text{Spin}}(\text{P}) = 1.007 e$ $\mu_e = 3.483 \text{ D}$
QCISD(T)/6-311++G(2d, 2f) $E_{\text{QCISD(T)}} = -1832.644015$ $R(\text{N-Zn}) = 4.380 \text{ \AA}^c$ $T_{e,\text{QCISD(T)}} = 0.0 \text{ eV}$	QCISD(T)/6-311++G(2d, 2f) $E_{\text{QCISD(T)}} = -1832.616903$ $R(\text{N-Zn}) = 1.841 \text{ \AA}^c$ $T_{e,\text{QCISD(T)}} = 0.738 \text{ eV}$	QCISD(T)/6-311++G(2d, 2f) $E_{\text{QCISD(T)}} = -2118.942273$ $R(\text{P-Zn}) = 2.549 \text{ \AA}^c$ $T_{e,\text{QCISD(T)}} = 0.0 \text{ eV}$	QCISD(T)/6-311++G(2d, 2f) $E_{\text{QCISD(T)}} = -2118.941617$ $R(\text{P-Zn}) = 4.371 \text{ \AA}^c$ $T_{e,\text{QCISD(T)}} = 0.018 \text{ eV}$	QCISD(T)/6-311++G(2d, 2f) $E_{\text{QCISD(T)}} = -2118.923840$ $R(\text{P-Zn}) = 2.213 \text{ \AA}^c$ $T_{e,\text{QCISD(T)}} = 0.502 \text{ eV}$

^a Short-bond minimum.^b Long-bond minimum.^c At QCISD/6-311++G(d, f) optimal geometry.

Table 9. Calculated molecular properties of the lowest OZn states.

OZn ($^1\Sigma^+$) $1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^2 2\pi^4 4\sigma^0$	OZn ($^3\Pi_i$) $1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^2 2\pi^3 4\sigma^1$	OZn ($^3\Sigma^-$) $1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^2 2\pi^2 4\sigma^2$	OZn ($^3\Sigma^+$) $1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^1 2\pi^4 4\sigma^1$
B3LYP/6-311++G(d, f) $E_{B3LYP} = -1854.486168$ $R_e(\text{O-Zn}) = 1.719 \text{ \AA}$ $\omega_e = 719 \text{ cm}^{-1}$	B3LYP/6-311++G(d, f) $E_{B3LYP} = -1854.490438$ $R_e(\text{O-Zn}) = 1.905 \text{ \AA}$ $\omega_e = 490 \text{ cm}^{-1}$ $\langle S^2 \rangle = 2.009$	B3LYP/6-311++G(d, f) $E_{B3LYP} = -1854.443378$ $R_e(\text{O-Zn}) = 5.646 \text{ \AA}$ $\omega_e = 6 \text{ cm}^{-1}$ $\langle S^2 \rangle = 2.003$	B3LYP/6-311++G(d, f) $E_{B3LYP} = -1854.430924$ $R_e(\text{O-Zn}) = 1.826 \text{ \AA}$ $\omega_e = 534 \text{ cm}^{-1}$ $\langle S^2 \rangle = 2.003$
$T_{e,B3LYP} = 0.0 \text{ eV}$	$T_{e,B3LYP} = -0.116 \text{ eV}$	$T_{e,B3LYP} = 1.164 \text{ eV}$	$T_{e,B3LYP} = 1.503 \text{ eV}$
MP2/6-311++G(d, f) $E_{PMP2} = -1853.078223$ $R_e(\text{O-Zn}) = 1.679 \text{ \AA}$ $\omega_e = 913 \text{ cm}^{-1}$	MP2/6-311++G(d, f) $E_{PMP2} = -1853.059511$ $R_e(\text{O-Zn}) = 1.858 \text{ \AA}$ $\omega_e = 555 \text{ cm}^{-1}$ $\langle S^2 \rangle = 2.020$	MP2/6-311++G(d, f) $E_{PMP2} = -1853.016020$ $R_e(\text{O-Zn}) = 4.494 \text{ \AA}$ $\omega_e = 16 \text{ cm}^{-1}$ $\langle S^2 \rangle = 2.008$	MP2/6-311++G(d, f) $E_{PMP2} = -1853.004254$ $R_e(\text{O-Zn}) = 1.816 \text{ \AA}$ $\omega_e = 563 \text{ cm}^{-1}$ $\langle S^2 \rangle = 2.008$
$T_{e,PMP2} = 0.0 \text{ eV}$	$T_{e,PMP2} = 0.509 \text{ eV}$	$T_{e,PMP2} = 1.693 \text{ eV}$	$T_{e,PMP2} = 2.013 \text{ eV}$
QCISD/6-311++G(d, f) $E_{QCISD} = -1853.0374961$ $R_e(\text{O-Zn}) = 1.733 \text{ \AA}$ $\omega_e = 690 \text{ cm}^{-1}$	QCISD/6-311++G(d, f) $E_{QCISD} = -1853.035992$ $R_e(\text{O-Zn}) = 1.873 \text{ \AA}$ $\omega_e = 525 \text{ cm}^{-1}$ $\langle S^2 \rangle = 2.022$	QCISD/6-311++G(d, f) $E_{QCISD} = -1853.000850$ $R_e(\text{O-Zn}) = 4.576 \text{ \AA}$ $\omega_e = 15 \text{ cm}^{-1}$ $\langle S^2 \rangle = 2.008$	QCISD/6-311++G(d, f) $E_{QCISD} = -1852.981934$ $R_e(\text{O-Zn}) = 1.818 \text{ \AA}$ $\omega_e = 561 \text{ cm}^{-1}$ $\langle S^2 \rangle = 2.008$
$T_{e,QCISD} = 0.0 \text{ eV}$ $Q^{\text{Mull}}(\text{O}) = -0.420 e$ $Q^{\text{NPA}}(\text{O}) = -1.094 e$	$T_{e,QCISD} = 0.041 \text{ eV}$ $Q^{\text{Mull}}(\text{O}) = -0.306 e$ $Q^{\text{NPA}}(\text{O}) = -0.735 e$ $Q^{\text{Spin}}(\text{O}) = 1.187 e$	$T_{e,QCISD} = 0.997 \text{ eV}$ $Q^{\text{Mull}}(\text{O}) = +0.003 e$ $Q^{\text{NPA}}(\text{O}) = -0.000 e$ $Q^{\text{Spin}}(\text{O}) = 2.000 e$	$T_{e,QCISD} = 1.512 \text{ eV}$ $Q^{\text{Mull}}(\text{O}) = -0.514 e$ $Q^{\text{NPA}}(\text{O}) = -0.913 e$ $Q^{\text{Spin}}(\text{O}) = 0.818 e$
$\mu_e = 5.374 \text{ D}$	$\mu_e = 2.613 \text{ D}$	$\mu_e = 0.075 \text{ D}$	$\mu_e = 3.124 \text{ D}$
QCISD(T)/6-311++G(2d, 2f) $E_{QCISD(T)} = -1853.143193$ $R(\text{O-Zn}) = 1.733 \text{ \AA}^a$ $T_{e,QCISD(T)} = 0.0 \text{ eV}$	QCISD(T)/6-311++G(2d, 2f) $E_{QCISD(T)} = -1853.135279$ $R(\text{O-Zn}) = 1.873 \text{ \AA}^a$ $T_{e,QCISD(T)} = 0.215 \text{ eV}$	QCISD(T)/6-311++G(2d, 2f) $E_{QCISD(T)} = -1853.094045$ $R(\text{O-Zn}) = 4.576 \text{ \AA}^a$ $T_{e,QCISD(T)} = 1.337 \text{ eV}$	QCISD(T)/6-311++G(2d, 2f) $E_{QCISD(T)} = -1853.081107$ $R(\text{O-Zn}) = 1.818 \text{ \AA}^a$ $T_{e,QCISD(T)} = 1.689 \text{ eV}$

^a At QCISD/6-311++G(d, f) optimal geometry.

2.38 eV experiment [2]) or of P (^2D , 1.41 eV experiment [2]), as a result of which the quartet $^4\Sigma^-$ state remains the ground state.

3.6. OZn and SZn

Early experimental dissociation energies of ZnO and ZnS were found to be relatively high: $D_0(\text{ZnO}) < 2.82 \text{ eV}$ [5] and $D_0(\text{ZnS}) = 2.08 \text{ eV}$ [5]. These experimental data were found to be in conflict with the *ab initio* predictions $D_0(\text{ZnO}) = 1.16 \text{ eV}$ and $D_0(\text{ZnS}) = 1.19 \text{ eV}$ obtained at the CPF level of theory with O (11s7p3d1f/6s4p3d1f) + Zn (14s11p6d4f/8s6p4d3f) basis sets. That disagreement between high quality *ab initio* calculation and experimental results is large and thus demands additional study. Clemmer, Dalleska and Armentrout recently reported $D_0(\text{ZnO}) = 1.61 \pm 0.04 \text{ eV}$ [18] using guided ion-beam mass spectrometry to measure the kinetic energy dependence of the endothermic reaction of Zn^+ with NO_2 . This D_0 is in much better agreement with the *ab initio* results by Bauschlicher and Langhoff [16], who

also performed CISD and CPF calculations for the four lowest $^1\Sigma^+$, $^3\Pi$, $^1\Pi$ and $^3\Sigma^+$ states of ZnO and ZnS. Only at the CPF level of theory was the ground state of ZnO found to be the singlet $^1\Sigma^+$, while the CISD method predicted the $^3\Pi$ state lower by 54 cm^{-1} than the $^1\Sigma^+$ state. For ZnS both methods predicted the $^1\Sigma^+$ ground electronic state.

We performed B3LYP, MP2 and QCISD geometry optimizations using 6-311++G(d, f) basis sets for four, $^1\Sigma^+$ ($1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^2 2\pi^4 4\sigma^0$), $^3\Pi_i$ ($1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^2 2\pi^3 4\sigma^1$), $^3\Sigma^-$ ($1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^2 2\pi^2 4\sigma^2$), and $^3\Sigma^+$ ($1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^1 2\pi^4 4\sigma^1$), electronic states of ZnO and ZnS. Our results are summarized in tables 9 and 10.

We found for both molecules that three states, $^1\Sigma^+$, $^3\Pi_i$ and $^3\Sigma^+$, have short bond lengths and high vibrational frequencies and therefore are chemically bound, while the $^3\Sigma^-$ state was found to be a weak van der Waals complex with long bonds and very low vibrational frequencies. The $^1\Sigma^+$ state was found to be the

Table 10. Calculated molecular properties of the lowest SZn states.

SZn ($^1\Sigma^+$) $1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^2 2\pi^4 4\sigma^0$	SZn ($^3\Pi_i$) $1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^2 2\pi^3 4\sigma^1$	SZn ($^3\Sigma^-$) $1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^2 2\pi^2 4\sigma^2$	SZn ($^3\Sigma^+$) $1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^1 2\pi^4 4\sigma^1$
B3LYP/6-311++G(d, f) $E_{B3LYP} = -2177.530717$ $R_e(\text{S-Zn}) = 2.083 \text{ \AA}$ $\omega_e = 434 \text{ cm}^{-1}$	B3LYP/6-311++G(d, f) $E_{B3LYP} = -2177.522536$ $R_e(\text{S-Zn}) = 2.303 \text{ \AA}$ $\omega_e = 287 \text{ cm}^{-1}$ $\langle S^2 \rangle = 2.006$	B3LYP/6-311++G(d, f) $E_{B3LYP} = -2177.486592$ $R_e(\text{S-Zn}) = 6.040 \text{ \AA}$ $\omega_e = 7 \text{ cm}^{-1}$ $\langle S^2 \rangle = 2.003$	B3LYP/6-311++G(d, f) $E_{B3LYP} = -2177.446350$ $R_e(\text{S-Zn}) = 2.253 \text{ \AA}$ $\omega_e = 309 \text{ cm}^{-1}$ $\langle S^2 \rangle = 2.004$
$T_{e,B3LYP} = 0.0 \text{ eV}$	$T_{e,B3LYP} = 0.222 \text{ eV}$	$T_{e,B3LYP} = 1.201 \text{ eV}$	$T_{e,B3LYP} = 2.296 \text{ eV}$
MP2/6-311++G(d, f) $E_{PMP2} = -2175.720773$ $R_e(\text{S-Zn}) = 2.048 \text{ \AA}$ $\omega_e = 478 \text{ cm}^{-1}$	MP2/6-311++G(d, f) $E_{PMP2} = -2175.710148$ $R_e(\text{S-Zn}) = 2.227 \text{ \AA}$ $\omega_e = 349 \text{ cm}^{-1}$ $\langle S^2 \rangle = 2.015$	MP2/6-311++G(d, f) $E_{PMP2} = -2175.675883$ $R_e(\text{S-Zn}) = 4.527 \text{ \AA}$ $\omega_e = 20 \text{ cm}^{-1}$ $\langle S^2 \rangle = 2.006$	MP2/6-311++G(d, f) $E_{PMP2} = -2175.637310$ $R_e(\text{S-Zn}) = 2.215 \text{ \AA}$ $\omega_e = 336 \text{ cm}^{-1}$ $\langle S^2 \rangle = 2.014$
$T_{e,PMP2} = 0.0 \text{ eV}$	$T_{e,PMP2} = 0.289 \text{ eV}$	$T_{e,PMP2} = 1.221 \text{ eV}$	$T_{e,PMP2} = 2.271 \text{ eV}$
QCISD/6-311++G(d, f) $E_{QCISD} = -2175.697996$ $R_e(\text{S-Zn}) = 2.074 \text{ \AA}$ $\omega_e = 447 \text{ cm}^{-1}$	QCISD/6-311++G(d, f) $E_{QCISD} = -2175.692800$ $R_e(\text{S-Zn}) = 2.257 \text{ \AA}$ $\omega_e = 329 \text{ cm}^{-1}$ $\langle S^2 \rangle = 2.016$	QCISD/6-311++G(d, f) $E_{QCISD} = -2175.664035$ $R_e(\text{S-Zn}) = 4.629 \text{ \AA}$ $\omega_e = 18 \text{ cm}^{-1}$ $\langle S^2 \rangle = 2.006$	QCISD/6-311++G(d, f) $E_{QCISD} = -2175.620919$ $R_e(\text{S-Zn}) = 2.227 \text{ \AA}$ $\omega_e = 335 \text{ cm}^{-1}$ $\langle S^2 \rangle = 2.014$
$T_{e,QCISD} = 0.0 \text{ eV}$ $Q^{\text{Mull}}(\text{S}) = -0.289 e$ $Q^{\text{NPA}}(\text{S}) = -0.960 e$	$T_{e,QCISD} = 0.141 \text{ eV}$ $Q^{\text{Mull}}(\text{S}) = -0.097 e$ $Q^{\text{NPA}}(\text{S}) = -0.583 e$ $Q^{\text{Spin}}(\text{S}) = 1.244 e$	$T_{e,QCISD} = 0.924 \text{ eV}$ $Q^{\text{Mull}}(\text{S}) = +0.008 e$ $Q^{\text{NPA}}(\text{S}) = +0.001 e$ $Q^{\text{Spin}}(\text{S}) = 2.002 e$	$T_{e,QCISD} = 2.097 \text{ eV}$ $Q^{\text{Mull}}(\text{S}) = -0.339 e$ $Q^{\text{NPA}}(\text{S}) = -0.811 e$ $Q^{\text{Spin}}(\text{S}) = 0.722 e$
$\mu_e = 5.223 \text{ D}$	$\mu_e = 1.811 \text{ D}$	$\mu_e = 0.158 \text{ D}$	$\mu_e = 2.825 \text{ D}$
QCISD(T)/6-311++G(2d, 2f) $E_{QCISD(T)} = -2175.800527$ $R(\text{S-Zn}) = 2.074 \text{ \AA}^a$ $T_{e,QCISD(T)} = 0.0 \text{ eV}$	QCISD(T)/6-311++G(2d, 2f) $E_{QCISD(T)} = -2175.790253$ $R(\text{S-Zn}) = 2.257 \text{ \AA}^a$ $T_{e,QCISD(T)} = 0.280 \text{ eV}$	QCISD(T)/6-311++G(2d, 2f) $E_{QCISD(T)} = -2175.760489$ $R(\text{S-Zn}) = 4.629 \text{ \AA}^a$ $T_{e,QCISD(T)} = 1.089 \text{ eV}$	QCISD(T)/6-311++G(2d, 2f) $E_{QCISD(T)} = -2175.719073$ $R(\text{S-Zn}) = 2.227 \text{ \AA}^a$ $T_{e,QCISD(T)} = 2.216 \text{ eV}$

^a At QCISD/6-311++G(d, f) optimal geometry.

ground electronic state for both molecules at all levels of theory except at the B3LYP/6-311++G(d, f) level for ZnO, in which case the $^3\Pi_i$ state was found to be lower than the $^1\Sigma^+$ state by 0.116 eV. Therefore, except for the B3LYP/6-311++G(d, f) method, the other two methods correctly predict the ground electronic state.

The molecular constants for the ground electronic states of ZnO and ZnS calculated at our best level of theory QCISD/6-311++G(d, f): $R_e(\text{Zn-O}) = 1.733 \text{ \AA}$, $\omega_e(\text{ZnO}) = 690 \text{ cm}^{-1}$, $R_e(\text{Zn-S}) = 2.074 \text{ \AA}$ and $\omega_e(\text{ZnS}) = 447 \text{ cm}^{-1}$ are in a good agreement with the CPF results: $R_e(\text{Zn-O}) = 1.771 \text{ \AA}$, $\omega_e(\text{ZnO}) = 646 \text{ cm}^{-1}$, $R_e(\text{Zn-S}) = 2.076 \text{ \AA}$ and $\omega_e(\text{ZnS}) = 460 \text{ cm}^{-1}$ and with the CISD results: $R_e(\text{Zn-O}) = 1.714 \text{ \AA}$, $\omega_e(\text{ZnO}) = 709 \text{ cm}^{-1}$, $R_e(\text{Zn-S}) = 2.060 \text{ \AA}$ and $\omega_e(\text{ZnS}) = 465 \text{ cm}^{-1}$ [16]. Therefore we conclude that QCISD/6-311++G(d, f) provides a reasonable compromise for obtaining molecular constants at reasonable cost. The dissociation energies $D_0(\text{ZnO}) = 1.30 \text{ eV}$ and $D_0(\text{ZnS}) = 1.06 \text{ eV}$

again are in good agreement with the CPF data of Bauschlicher and Langhoff [16], and strongly support the lower $D_0(\text{ZnO}) = 1.61 \pm 0.04 \text{ eV}$ experimental dissociation energy obtained by Clemmer, Dalleska and Armentrout [18]. Our harmonic frequency $\omega_e(\text{ZnO}) = 690 \text{ cm}^{-1}$ is somewhat lower than the experimental finding $\Delta G_{1/2} = 769.2 \text{ cm}^{-1}$ for ^{64}ZnO in a solid argon matrix by Chertihin and Andrews [21]. Still we consider this agreement as fair taking into account the modest basis sets in our calculations and the multiconfigurational nature of the ZnO ground singlet state. The large dipole moments (5.37 D for ZnO and 5.22 D for ZnS) show that significant charge flow from Zn to O or S exists in the ground state.

Oxygen and sulphur atoms correlate in their ^3P ground electronic state with the ground electronic state of Zn to form $^3\Pi_i$ or $^3\Sigma^-$ states, and not the singlet $^1\Sigma^+$ ground electronic state. Therefore, the intrinsic dissociation energies of ZnO and ZnS must be calculated relative to the ^1D state of O or S and to the ^1S state of Zn.

Table 11. Calculated molecular properties of the lowest FZn and ClZn states.

FZn ($^2\Sigma^+$) $1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^2 2\pi^4 4\sigma^1$	FZn ($^2\Pi_i$) $1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^2 2\pi^3 4\sigma^2$	ClZn ($^2\Sigma^+$) $1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^2 2\pi^4 4\sigma^1$	ClZn ($^2\Pi_i$) $1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^2 2\pi^3 4\sigma^2$
B3LYP/6-311++G(d, f) $E_{B3LYP} = -1879.218\,910$ $R_e(\text{F-Zn}) = 1.814\text{ \AA}$ $\omega_e = 562\text{ cm}^{-1}$ $\langle S^2 \rangle = 0.752$ $T_{e,B3LYP} = 0.0\text{ eV}$	B3LYP/6-311++G(d, f) $E_{B3LYP} = -1879.114\,075$ $R_e(\text{F-Zn}) = 4.886\text{ \AA}$ $\omega_e = 9\text{ cm}^{-1}$ $\langle S^2 \rangle = 0.751$ $T_{e,B3LYP} = 2.853\text{ eV}$	B3LYP/6-311++G(d, f) $E_{B3LYP} = -2239.594\,160$ $R_e(\text{Cl-Zn}) = 2.197\text{ \AA}$ $\omega_e = 354\text{ cm}^{-1}$ $\langle S^2 \rangle = 0.752$ $T_{e,B3LYP} = 0.0\text{ eV}$	B3LYP/6-311++G(d, f) $E_{B3LYP} = -2239.520\,422$ $R_e(\text{Cl-Zn}) = 5.900\text{ \AA}$ $\omega_e = 10\text{ cm}^{-1}$ $\langle S^2 \rangle = 0.752$ $T_{e,B3LYP} = 2.006\text{ eV}$
MP2/6-311++G(d, f) $E_{PMP2} = -1877.768\,227$ $R_e(\text{F-Zn}) = 1.793\text{ \AA}$ $\omega_e = 595\text{ cm}^{-1}$ $\langle S^2 \rangle = 0.753$ $T_{e,PMP2} = 0.0\text{ eV}$	MP2/6-311++G(d, f) $E_{PMP2} = -1877.653\,447$ $R_e(\text{F-Zn}) = 4.429\text{ \AA}$ $\omega_e = 14\text{ cm}^{-1}$ $\langle S^2 \rangle = 0.753$ $T_{e,PMP2} = 3.123\text{ eV}$	MP2/6-311++G(d, f) $E_{PMP2} = -2237.761\,140$ $R_e(\text{Cl-Zn}) = 2.137\text{ \AA}$ $\omega_e = 397\text{ cm}^{-1}$ $\langle S^2 \rangle = 0.754$ $T_{e,PMP2} = 0.0\text{ eV}$	MP2/6-311++G(d, f) $E_{PMP2} = -2237.680\,149$ $R_e(\text{Cl-Zn}) = 4.519\text{ \AA}$ $\omega_e = 11\text{ cm}^{-1}$ $\langle S^2 \rangle = 0.755$ $T_{e,PMP2} = 2.203\text{ eV}$
QCISD/6-311++G(d, f) $E_{QCISD} = -1877.734\,275$ $R_e(\text{F-Zn}) = 1.796\text{ \AA}$ $\omega_e = 593\text{ cm}^{-1}$ $\langle S^2 \rangle = 0.753$ $T_{e,QCISD} = 0.0\text{ eV}$ $Q^{\text{Mull}}(\text{F}) = -0.472\text{ e}$ $Q^{\text{NPA}}(\text{F}) = -0.862\text{ e}$ $Q^{\text{Spin}}(\text{F}) = 0.056\text{ e}$ $\mu_e = 3.241\text{ D}$	QCISD/6-311++G(d, f) $E_{QCISD} = -1877.633\,828$ $R_e(\text{F-Zn}) = 4.509\text{ \AA}$ $\omega_e = 13\text{ cm}^{-1}$ $\langle S^2 \rangle = 0.753$ $T_{e,QCISD} = 2.733\text{ eV}$ $Q^{\text{Mull}}(\text{F}) = +0.002\text{ e}$ $Q^{\text{NPA}}(\text{F}) = +0.000\text{ e}$ $Q^{\text{Spin}}(\text{F}) = 1.000\text{ e}$ $\mu_e = 0.037\text{ D}$	QCISD/6-311++G(d, f) $E_{QCISD} = -2237.739\,477$ $R_e(\text{Cl-Zn}) = 2.156\text{ \AA}$ $\omega_e = 386\text{ cm}^{-1}$ $\langle S^2 \rangle = 0.754$ $T_{e,QCISD} = 0.0\text{ eV}$ $Q^{\text{Mull}}(\text{Cl}) = -0.212\text{ e}$ $Q^{\text{NPA}}(\text{Cl}) = -0.740\text{ e}$ $Q^{\text{Spin}}(\text{Cl}) = 0.112\text{ e}$ $\mu_e = 2.782\text{ D}$	QCISD/6-311++G(d, f) $E_{QCISD} = -2237.667\,097$ $R_e(\text{Cl-Zn}) = 4.685\text{ \AA}$ $\omega_e = 14\text{ cm}^{-1}$ $\langle S^2 \rangle = 0.755$ $T_{e,QCISD} = 1.969\text{ eV}$ $Q^{\text{Mull}}(\text{Cl}) = +0.006\text{ e}$ $Q^{\text{NPA}}(\text{Cl}) = +0.000\text{ e}$ $Q^{\text{Spin}}(\text{Cl}) = 1.000\text{ e}$ $\mu_e = 0.078\text{ D}$
QCISD(T)/6-311++G(2d, 2f) $E_{QCISD(T)} = -1877.840\,316$ $R(\text{F-Zn}) = 1.796\text{ \AA}^a$ $T_{e,QCISD(T)} = 0.0\text{ eV}$	QCISD(T)/6-311++G(2d, 2f) $E_{QCISD(T)} = -1877.732\,707$ $R(\text{F-Zn}) = 4.509\text{ \AA}^a$ $T_{e,QCISD(T)} = 2.928\text{ eV}$	QCISD(T)/6-311++G(2d, 2f) $E_{QCISD(T)} = -2237.840\,968$ $R(\text{Cl-Zn}) = 2.156\text{ \AA}^a$ $T_{e,QCISD(T)} = 0.0\text{ eV}$	QCISD(T)/6-311++G(2d, 2f) $E_{QCISD(T)} = -2237.766\,785$ $R(\text{Cl-Zn}) = 4.685\text{ \AA}^a$ $T_{e,QCISD(T)} = 2.019\text{ eV}$

^a At QCISD/6-311++G(d, f) optimal geometry.

Using the experimental $^3\text{P}^1\text{D}$ excitation energies for the O (1.97 eV) or S (1.15 eV) from [2] and our computed dissociation energies for ZnO and ZnS, we estimated intrinsic bond energies of the ground electronic states of ZnO and ZnS to be 3.306 eV and 2.244 eV, respectively. The calculated intrinsic dissociation energies for the $^3\Pi_i$ and $^3\Sigma$ states, which correlate with the atomic ground state asymptotes, were found to be 1.13 eV (ZnO, $^3\Pi_i$), 0.005 eV (ZnO, $^3\Sigma^-$), 0.82 eV (ZnS, $^3\Pi_i$) and 0.012 eV (ZnS, $^3\Sigma^-$). Therefore, strong chemical bonding in the singlet state wins the competition with the required excitation energy of O and S, as a result of which ZnO and ZnS are strongly chemically bound molecules with short bond lengths, large dipole moments, and high vibrational frequencies.

3.7. FZn and ClZn

Experimental data on these molecules are scarce [3, 4, 5]. The dissociation energy $D_0 = 2.1\text{ eV}$ is known for ClZn [5], and the vibrational frequencies are known

for FZn and ClZn [5, 27]. Bowmaker and Schwerdtfeger [25] recently performed MP2 and CISDSC calculations on FZn and ClZn in their ground electronic states using relatively large valence basis sets and pseudopotentials to describe the core electrons on Zn. We performed all-electron B3LYP, MP2 and QCISD calculations for the two lowest $^2\Sigma^+$ and $^2\Pi_i$ states of FZn and ClZn. The results of our calculations are presented in table 11.

Fluorine and chlorine atoms have $2s^2 2p^5$ (F) and $3s^2 3p^5$ (Cl) valence electronic configurations, so one expects $^2\Pi_i$ or $^2\Sigma^+$ low lying electronic states (depending on the orientation of the 2p or 3p orbital hole). The $^2\Sigma^+$ states were found to be strongly bound, whereas the $^2\Pi_i$ states are van der Waals complexes for both molecules. At all levels of theory, the $^2\Sigma^+$ state was found to be the ground electronic state for FZn and ClZn. At our highest level of theory (QCISD(T)/6-311++G(2d, 2f)) the $^2\Pi_i$ states are 2.93 eV (FZn) and 2.02 eV (ClZn) higher in energy, and therefore the $^2\Sigma^+$ ground electronic state is well established for both molecules.

Table 12. Calculated dissociation energies and dipole moments.

Reaction	D_e (eV) ^a	D_0 (eV) ^{a,b}	μ_e (D) ^c
LiZn ($^2\Sigma^+$) \rightarrow Li (2S) + Zn (1S)	0.084	0.077	0.074
BeZn ($^1\Sigma^+$) \rightarrow Be (1S) + Zn (1S)	0.014	0.013	0.003
BZn ($^2\Pi_r$) \rightarrow B (2P) + Zn (1S)	0.252	0.237	1.439
CZn ($^3\Sigma^-$) \rightarrow C (3P) + Zn (1S)	0.923	0.893	2.771
NZn ($^4\Sigma^-$) \rightarrow N (4S) + Zn (1S)	0.007	0.006	0.016
OZn ($^1\Sigma^+$) \rightarrow O (3P) + Zn (1S)	1.339	1.296	5.374
FZn ($^2\Sigma^+$) \rightarrow F (2P) + Zn (1S)	2.931	2.894	3.241
NeZn ($^1\Sigma^+$) \rightarrow Ne (1S) + Zn (1S)	0.004	0.003	0.012
NaZn ($^2\Sigma^+$) \rightarrow Na (2S) + Zn (1S)	0.042	0.040	0.008
MgZn ($^1\Sigma^+$) \rightarrow Mg (1S) + Zn (1S)	0.019	0.018	0.004
AlZn ($^2\Pi_r$) \rightarrow Al (2P) + Zn (1S)	0.177	0.148	0.731
SiZn ($^3\Sigma^-$) \rightarrow Si (3P) + Zn (1S)	0.591	0.577	2.121
PZn ($^4\Sigma^-$) \rightarrow P (4S) + Zn (1S)	0.034 ^d	0.026 ^d	0.336 ^d
SZn ($^1\Sigma^+$) \rightarrow S (3P) + Zn (1S)	1.099	1.058	5.223
ClZn ($^2\Sigma^+$) \rightarrow Cl (2P) + Zn (1S)	2.027	2.003	2.782
ArZn ($^1\Sigma^+$) \rightarrow Ar (1S) + Zn (1S)	0.005	0.004	0.016

^a D_e calculated at the QCISD(T)/6-311++(2d, 2f)//QCISD/6-311++G(d, f) level of theory.

^b Zero point energy correction calculated at the QCISD/6-311++G(d, f) level of theory.

^c μ_e calculated at the QCISD(T)/6-311++(2d, 2f) level of theory.

^d Data for the short-bond minimum (see the text).

The calculated dissociation energies $D_0(\text{FZn}) = 2.89$ eV and $D_0(\text{ClZn}) = 2.00$ eV (see table 12) demonstrate the chemical bonding in these molecules and the large dipole moments illustrate the significant charge transfer in the $^2\Sigma^+$ states. Our calculated dissociation energy of ClZn is in excellent agreement with the experimental $D_0(\text{ClZn}) = 2.1$ eV [5] value, but our dissociation energies are substantially larger than $D_e(\text{FZn}) = 2.03$ eV and $D_e(\text{ClZn}) = 1.81$ eV obtained by Bowmaker and Schwerdtfeger [25]. However, our optimal bond lengths $R_e(\text{F—Zn}) = 1.796$ Å and $R_e(\text{Cl—Zn}) = 2.156$ Å agree well with the CISDSC results: $R_e(\text{F—Zn}) = 1.787$ Å and $R_e(\text{Cl—Zn}) = 2.169$ Å [25]. Our QCISD harmonic frequencies $\omega_e(\text{FZn}) = 593$ cm⁻¹ and $\omega_e(\text{ClZn}) = 386$ cm⁻¹ are in fair agreement with the experimental data: $\omega_e(\text{FZn}) = 628$ cm⁻¹ and $\omega_e(\text{ClZn}) = 390.5$ cm⁻¹ [5].

3.8. NeZn and ArZn

The ArZn molecule was studied experimentally in its ground and excited electronic states [28, 29, 32]. Breckenridge and coworkers [28] found that ArZn in its $^1\Sigma^+$ ground electronic state is a very weak van der Waals complex with equilibrium bond length, dissociation energy and harmonic vibrational frequency of 4.18 Å, 0.012 eV and 20.5 cm⁻¹, respectively. There are no *ab initio* data on NeZn or ArZn according to the *Spectroscopic References for Diatomic Molecules* [4].

We performed *ab initio* calculations using B3LYP, MP2 and QCISD methods only for the ground $^1\Sigma^+$ electronic states and our results are reported in table 13.

The results of our calculations vary dramatically among these three methods. At our best QCISD level, the optimized bond length, dissociation energy and harmonic vibrational frequency of ArZn were found to be 4.80 Å, 0.005 eV and 11 cm⁻¹, respectively. Our potential is somewhat softer than the experimental potential of Breckenridge and coworkers [28]. This is probably a result of the moderate size of our basis sets, which would need to be very large to reproduce van der Waals potentials accurately. We expect about the same accuracy for the NeZn molecule, where experimental data are not yet available.

4. Overview

We performed systematic *ab initio* calculations at three (B3LYP, MP2 and QCISD) levels of theory of the bonding between Zn atoms and all first- and second-row main group atoms. When chemical bonding occurs in the ground or excited states, all three methods produce very similar results, which are in good agreement with available experimental data (except the vibrational frequency of AlZn). However, the computational results vary dramatically when only weak van der Waals bonding occurs in the ground or excited states.

We computationally predicted the ground electronic states for all ZnX (X = Li–Ne; Na–Ar) diatomic mole-

Table 13. Calculated molecular properties of NeZn and ArZn.

NeZn ($^1\Sigma^+$) $1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^2 2\pi^4 4\sigma^2$	ArZn ($^1\Sigma^+$) $1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^2 2\pi^4 4\sigma^2$
B3LYP/6-311++G(d, f) $E_{\text{B3LYP}} = -1908.313896$ $R_c(\text{Ne-Zn}) = 4.348 \text{ \AA}$ $\omega_e = 16 \text{ cm}^{-1}$	B3LYP/6-311++G(d, f) $E_{\text{B3LYP}} = -2306.907377$ $R_c(\text{Ar-Zn}) = 5.939 \text{ \AA}$ $\omega_e = 8 \text{ cm}^{-1}$
MP2/6-311++G(d, f) $E_{\text{PMP2}} = -1906.831776$ $R_c(\text{Ne-Zn}) = 4.404 \text{ \AA}$ $\omega_e = 13 \text{ cm}^{-1}$	MP2/6-311++G(d, f) $E_{\text{PMP2}} = -2305.047377$ $R_c(\text{Ar-Zn}) = 4.592 \text{ \AA}$ $\omega_e = 13 \text{ cm}^{-1}$
QCISD/6-311++G(d, f) $E_{\text{QCISD}} = -1906.804723$ $R_c(\text{Ne-Zn}) = 4.480 \text{ \AA}$ $\omega_e = 12 \text{ cm}^{-1}$ $Q^{\text{Mull}}(\text{Ne}) = +0.001 e$ $Q^{\text{NPA}}(\text{Ne}) = +0.000 e$ $\mu_e = 0.012 \text{ D}$	QCISD/6-311++G(d, f) $E_{\text{QCISD}} = -2305.030814$ $R_c(\text{Ar-Zn}) = 4.803 \text{ \AA}$ $\omega_e = 11 \text{ cm}^{-1}$ $Q^{\text{Mull}}(\text{Ar}) = +0.001 e$ $Q^{\text{NPA}}(\text{Ar}) = +0.000 e$ $\mu_e = 0.016 \text{ D}$
QCISD(T)/6-311++G(2d, 2f) $E_{\text{QCISD(T)}} = -1906.909040$ $R(\text{Ne-Zn}) = 4.480 \text{ \AA}^a$	QCISD(T)/6-311++G(2d, 2f) $E_{\text{QCISD(T)}} = -2305.134150$ $R(\text{Ar-Zn}) = 4.803 \text{ \AA}^a$

^a At QCISD/6-311++G(d, f) optimal geometry.

cules. In our *Periodic Table of Diatomic Molecules*, Part B, *Diatomics Composed from One Main Group Atom and One Transition Metal Atom* [3], we assumed the canonical order of the valence molecular orbitals to be $1\sigma 2\sigma 1\pi 1\delta 3\sigma 2\pi 4\sigma$ in order to use the Aufbau principle to predict the ground electronic states. According to this order of valence MOs, one arrives at the following ground electronic states: $^2\Sigma^+$ ($1\sigma^2 2\sigma^2 1\pi^4 1\delta^4 3\sigma^1 2\pi^0 4\sigma^0$) for LiZn and NaZn; $^1\Sigma^+$ ($1\sigma^2 2\sigma^2 1\pi^4 1\delta^4 3\sigma^2 2\pi^0 4\sigma^0$) for BeZn and MgZn; $^2\Pi_i$ ($1\sigma^2 2\sigma^2 1\pi^4 1\delta^4 3\sigma^2 2\pi^1 4\sigma^0$) for BZn and AlZn; $^3\Sigma^-$ ($1\sigma^2 2\sigma^2 1\pi^4 1\delta^4 3\sigma^2 2\pi^2 4\sigma^0$) for CZn and SiZn; $^2\Pi_i$ ($1\sigma^2 2\sigma^2 1\pi^4 1\delta^4 3\sigma^2 2\pi^3 4\sigma^0$) for NZn and PZn; $^1\Sigma^+$ ($1\sigma^2 2\sigma^2 1\pi^4 1\delta^4 3\sigma^2 2\pi^4 4\sigma^0$) for OZn and SZn; $^2\Sigma^+$ ($1\sigma^2 2\sigma^2 1\pi^4 1\delta^4 3\sigma^2 2\pi^4 4\sigma^1$) for FZn and ClZn, and $^1\Sigma^+$ ($1\sigma^2 2\sigma^2 1\pi^4 1\delta^4 3\sigma^2 2\pi^4 4\sigma^2$) for NeZn and ArZn. The ground electronic states found in this study agree with the Aufbau predictions except for NZn and PZn, where the high-spin $^4\Sigma^-$ states were found to be lower than the $^2\Pi_i$ states.

As expected, the bond strengths tend to increase as one moves from left to right in the period table as do the accompanying charge transfer and dipole moments. Within this general trend, a more substantial effect manifests itself. Those atoms that can present to the $4s^2$ Zn atom a p orbital occupancy in which the p_π orbitals are maximally occupied produce especially strong bonds.

For example, C (3P , $p_\pi^2 p_\sigma^0$), O (1D , $p_\pi^4 p_\sigma^0$), F (2P , $p_\pi^5 p_\sigma^1$), can do so, although for O (1D) it requires 2 eV to promote from O (3P , $p_\pi^3 p_\sigma^1$) to O (1D , $p_\pi^4 p_\sigma^0$) but this cost is more than offset by the strong Zn—O intrinsic bond. For N (4S , $p_\pi^2 p_\sigma^1$) promotion to N (2D , $p_\pi^3 p_\sigma^0$) produces the $^2\Pi_i$ state of ZnN, which does have a favourable p_π orbital occupancy. Indeed the $^2\Pi_i$ state of ZnN has a strong intrinsic bond but not strong enough to overcome the 4S — 2D promotion energy.

The importance of the orientation of the empty (for the first half of the period) or semi-occupied (for the second half of the period) p orbital of the X atom can be seen also in the bonding of BZn, AlZn, FZn and ClZn. When B ($p_\pi^1 p_\sigma^0$) or Al ($p_\pi^1 p_\sigma^0$) orientation occurs, strong chemical bonds are formed in the $^2\Pi_i$ states of BZn and AlZn. On the other hand, when B ($p_\pi^0 p_\sigma^1$) or Al ($p_\pi^0 p_\sigma^1$) orientation takes place, only weak van der Waals bonds are formed in the $^2\Sigma^+$ states of BZn and AlZn. Similarly, when F ($p_\pi^4 p_\sigma^1$) or Cl ($p_\pi^4 p_\sigma^1$) orientation occurs, strong chemical bonds are formed in the $^2\Sigma^+$ states of FZn and ClZn, and when F ($p_\pi^3 p_\sigma^2$) or Cl ($p_\pi^3 p_\sigma^2$) orientation takes place, only weak van der Waals bonds are formed in the $^2\Pi_i$ states of FZn and ClZn.

In the introduction we mentioned that data on diatomics composed of a transition a metal atom and a main group element are scarce [3, 4]. We hope that the success of the QCISD/6-311++G(d, f) data for geometries and frequencies and QCISD(T)/6-311++G(2d, 2f) data for excitation and dissociation energies, presented here, will help complete the determination of the ground electronic states and molecular constants of such diatomics.

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