Structure and Energetics of Gaseous HZnCl

Ioannis S. K. Kerkines,*,† Aristides Mavridis,*,† and Paraskevas A. Karipidis‡

Laboratory of Physical Chemistry, Department of Chemistry, National and Kapodistrian University of Athens, P.O. Box 64 004, 157 10 Zografou, Athens, Greece, and Laboratory of Applied Quantum Chemistry, Department of Chemistry, Aristotle University of Thessaloniki, 541 24 Thessaloniki, Greece

The HZnCl molecule has recently been observed both in the gas phase and in argon matrixes, and the complexity of its spectrum has created big discrepancies between experimental and theoretically predicted Zn−H bond distances. In an attempt to resolve the questionable H−ZnCl bond length issue, as well as to study its stability relative to bond breakage, we have investigated at a very high ab initio level its geometric and energetic parameters. At the coupled cluster level of theory [CCSD(T)] with the new correlation-consistent basis sets for Zn by Balabanov and Peterson, and with the inclusion of core/valence and one-electron Douglas−Kroll−Hess relativistic effects, the basis set extrapolated H−ZnCl and HZn−Cl bond lengths have been calculated to be 1.499 and 2.079 Å, compared with the experimental estimates of 1.596−1.789 and 2.08346 Å, respectively. With the same procedure, the experimentally unknown bond length of ground-state ZnCl has been found to be equal to 2.122 Å. As in the free diatomics ZnCl and ZnH, the HZn−Cl bond is stronger than the H−ZnCl bond by about 30 kcal/mol.

1. Introduction

Recently,[1] Macrae et al. prepared HZnCl, HCdCl, and HHgCl in Ar cold matrixes and obtained their IR spectrum, where it was shown that all three molecules are linear in their ground states. In more recent work,[2] Yu et al. obtained the same result for gas-phase HZnCl. In particular, Macrae et al. observed the three normal modes of vibration at 1952.3 [$\nu_1(\sigma^+) = \nu(Zn-H)$], 449.6 [$\nu_2(\pi^+) = \delta(H-Zn-Cl)$], and ~420 cm^{-1} [$\nu_3(\sigma^+) = \nu(Zn-Cl)$] with assignments pointed out by isotopic substitution and density functional theory (DFT) calculations. Corresponding values obtained for DZnCl were 1406.6, ~420, and 323.5 cm^{-1}. In the absence of rotational analysis of the IR spectrum, no experimental data were extracted for the bond lengths and, of course, bond dissociation energies for HZnCl. DFT calculations by the same group[1] using a CEP-31G basis set[3] predicted the molecule linear with bond lengths $r_{H-ZnCl} = 1.156$ Å and $r_{HZn-Cl} = 2.151$ Å.

On the other hand, Yu et al. were able to obtain the vibration−rotation emission spectrum of gaseous HZnCl for the $\nu_1(\sigma^+)$ normal mode.[2] These authors observed a very dense emission IR spectrum with the band origin at 1966.87 cm^{-1}. The density of the spectrum was considerable due to the rather small value of the rotational constant $2B$ (~0.3 cm^{-1}) and the number of observed HZnCl natural isotopomers (H^{64}Zn^{35}Cl, H^{66}Zn^{35}Cl, H^{68}Zn^{35}Cl, and H^{64}Zn^{37}Cl). This complexity rendered the analysis of the spectrum very difficult and finally J assignments were made through the guidance of DFT calculations. In turn, this created many uncertainties since an accurate value for the H−ZnCl bond distance could not be obtained (values ranged

from 1.596 to 1.789 Å), with the HZn−Cl bond length being somewhat more consistent, narrowed down in the range of 2.079 to 2.088 Å. Finally, a value of $r_{HZn-Cl} = 2.08346$ Å was obtained by use of the Kraitchman equation for linear molecules,[4] and the authors consider it as their best predicted value. However, by using this value in the moment of inertia and the center of mass equations, Yu et al. obtained rather large values for the H−ZnCl distance, namely, $r_{H-ZnCl} = 1.70480$ and 1.75796 Å, respectively.

Since a rather accurate estimate of the H−ZnCl bond length as well as the relative bond strengths and atomization energy of HZnCl are not yet known, we attempt to perform high-level ab initio calculations to obtain reliable values for these properties for the first time. Given this opportunity, we also present accurate estimates for some experimentally unknown properties for the ZnH and ZnCl fragments, that is, their dipole moments and the bond length of ground-state ZnCl. Finally, we also get a chance to observe the convergence properties of the new correlation-consistent basis sets of Balabanov and Peterson for the 1st transition metal row (Sc−Zn).[5]

2. Methodology

Our calculations were performed with the spin-restricted coupled cluster method with single, double, and a noniterative estimate of triple excitations, RCCSD(T).[6] For all atoms, we have used the correlation-consistent (cc) polarized valence basis sets of Dunning (H, Cl) and Balabanov and Peterson (Zn) of $n$tuple-ζ quality cc-pVnZ, where n = T, Q, and 5.[5,7] Calculations with these basis sets involve 20 valence electrons (3d^{10}4s^2 of Zn, 3s^{2}3p^5 of Cl and 1s^1 of H). The effect of the 3s^{2}3p^6 and 2s^{2}2p^6 electron cores of Zn and Cl, respectively, was accounted for with the use of the "weighted core" (wC) cc basis sets of $n$tuple-ζ quality, cc-pwCVnZ, n =T, Q, and 5.[5,8] One-electron relativistic effects were estimated within the second-order

* To whom correspondence should be addressed. E-mail: kerkines@chem.uoa.gr; mavridis@chem.uoa.gr.
† National and Kapodistrian University of Athens.
‡ Aristotle University of Thessaloniki.

Douglas−Kroll−Hess approximation (DKH)[9] and the corresponding cc-pVnZ-DKH basis sets, n = T, Q, and 5.[5,10] Complete basis set (CBS) limit properties were obtained with the mixed exponential/Gaussian extrapolation formula[11]
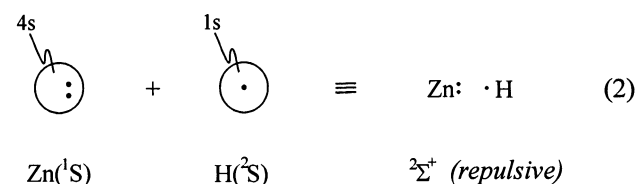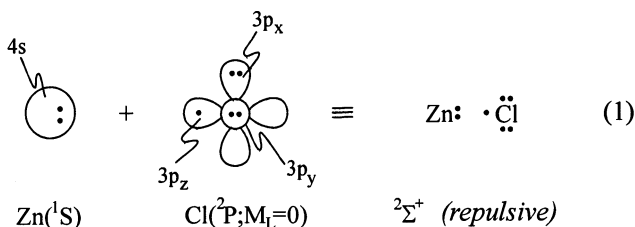
$$P_n = P_\infty + Ae^{-(n-1)} + Be^{-(n-1)^2} \qquad (1)$$

where P is a generic property, P_∞ its CBS limit, n the cardinal basis set number, while A and B are freely adjustable parameters. To these CBS values, an atomic spin−orbit correction taken from experiment was added where appropriate.

As the cardinal basis set number n was increased, our calculations produced binding energies and bond lengths with oscillatory behavior implying participation of pertinent basis set superposition errors (BSSE). Indeed, extrapolations to the CBS limits were possible only after the elimination of BSSE effects with the counterpoise technique.[12]
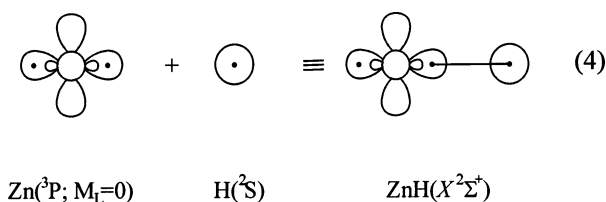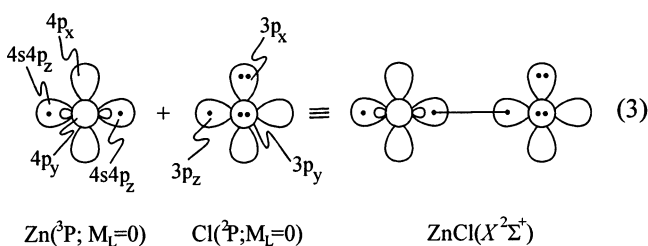
All calculations were performed with the MOLPRO 2002.6 package.[13]

3. Results and Discussion

3.a. ZnH and ZnCl. To calculate the H−ZnCl and HZn−Cl bond strengths as well as the atomization energy of HZnCl, calculations were performed for the ZnH (X $^2\Sigma^+$) and ZnCl (X $^2\Sigma^+$) ground states. The interaction of ground-state Zn with either Cl(^{2}P) or H(^{2}S) is expected to lead to repulsive or van der Waals attractive $^2\Sigma^+$ states according to the following valence-bond-Lewis (vbL) diagrams

However, excitation of Zn to its first excited state (^{3}P; $4s^14p^1$) creates the necessary conditions for bonding, succinctly shown by vbL diagrams 3 and 4

The ground X $^2\Sigma^+$ states of both ZnH and ZnCl carry the excited ^{3}P state character of Zn due to the interaction (avoided crossing) between the two aforementioned $^2\Sigma^+$ states for each molecule.

Table 1 shows fragment energies, as well as the ^{3}P ← ^{1}S Zn energy gap calculated at various levels of theory. At the RCCSD(T)/cc-pwCV∞Z CBS limit, this gap is predicted to be 3.874 eV. DKH relativistic effects are shown to be necessary in bringing the computed value in accord with experiment, 4.065 vs 4.054 eV.[14]

Table 2 summarizes our results for the ground-state ZnH and ZnCl diatomics. The ground states for both molecules have been extensively studied in the past, however the absence of an experimental bond length for ZnCl (X $^2\Sigma^+$) is somewhat startling. The BSSE-corrected binding energy of ZnH (X $^2\Sigma^+$) at the CBS limit of valence-only basis sets is 23.03 kcal/mol with respect to Zn($3d^{10}4s^2$; ^{1}S) + H(^{2}S) and 111.69 kcal/mol with respect to the *diabatic* Zn($3d^{10}4s^14p^1$; ^{3}P) + H(^{1}S) fragments. DKH relativistic effects seem to contribute the largest correction to these binding energies, fixing inter alia the ^{3}P ← ^{1}S energy gap of Zn (Table 1). Core/valence effects from the $3s^23p^6$ electron core of Zn contribute −0.64 and +0.23 kcal/mol to the binding energy, depending on the dissociation fragments. Furthermore, the experimental atomic-spin−orbit splitting[14] is included in the case of the Zn(^{3}P) + H(^{1}S) diabatic fragments. Taking into account all of the above, a "best value", D_e = 21.2 kcal/mol, is obtained, which is in close agreement with the experimentally reported value $D_e = D_0 + (\omega_e/2 - \omega_e x_e/4) = 0.85$ eV + (1607.6/2 − 55.14/4) cm^{-1} = 21.88 kcal/mol.[15,16] This experimental value may have an error bar of ±0.46 kcal/mol.[16] The corresponding value with respect to the diabatic fragments is 114.3 kcal/mol. Following a similar procedure, the best bond length value for ZnH (X $^2\Sigma^+$) is 1.588 Å, less than a hundredth of an angstrom from the experimental value of 1.5949.[15] We also note that, compared with the nonrelativistic valence limit, DKH relativistic effects reduce the bond distance by about 0.012 Å, while the $3s^23p^6$ core increases it by only 0.002 Å. A dipole moment of 0.59 D is also predicted for the ground state of ZnH, in agreement with previous theoretical results at the (modified) coupled-pair functional level(s).[21]

The binding energies of the X $^2\Sigma^+$ state of ZnCl at the cc-pV∞Z limit are 53.38 and 142.03 kcal/mol, depending on the dissociation limits, either Zn(^{1}S) + Cl(^{3}P) or Zn(^{3}P) + Cl(^{3}P). The σ bond in ZnCl is stronger than the σ bond in ZnH by about 30 kcal/mol, reflecting in part the larger ionicity of the former vs the latter molecule (Zn carrying a +0.60 vs +0.35 Mulliken charge at the Hartree−Fock level). The $(3s^23p^6)_{Zn}$ and $(2s^22p^6)_{Cl}$ electron cores contribute only slightly to the binding energy: −0.21 and +0.38 kcal/mol, respectively. Again, we find that DKH relativistic effects play a substantial role in affecting the binding energy, −3.12 and −1.25 kcal/mol, reflecting in large part the adjustment of the ^{3}P ← ^{1}S energy gap in Zn. Assuming additivity of core/valence, relativistic, and spin−orbit effects (the latter now originating from both Zn(^{3}P) and Cl(^{3}P)), we obtain our final best D_e values of 49.5 and 142.6 kcal/mol. The former value is closest to the oldest experimental value of 49.0 kcal/mol obtained from chemiluminescence measurements in Na/ZnCl flames.[15,20] More recent thermochemical results[17−19] have indicated that the Zn−Cl bond is slightly stronger, in the range of 53−56 kcal/mol. We believe that there is a fair agreement between our result and the thermochemical values. Our best equilibrium bond distance for ZnCl (X $^2\Sigma^+$) is 2.122 Å, affected by both relativistic (−0.0171 Å) and core/valence

Structure and Energetics of Gaseous HZnCl

J. Phys. Chem. A, Vol. 110, No. 37, 2006 **10901**

TABLE 1: Energies E (E_h) of H(^{1}S), Cl(^{2}P), Zn(^{1}S, ^{3}P), and the Zn ^{3}P $\leftarrow$ ^{1}S Separation Energy (eV) at the RCCSD(T) Level of Theory Using the TQ5 Sequence of Correlation-Consistent Basis Sets

basis set[a]	E (H, ^{1}S)	E (Cl, ^{2}P)	E (Zn, ^{1}S)	E (Zn, ^{3}P)	Zn ^{3}P $\leftarrow$ ^{1}S
cc-pVTZ	−0.499810	−459.671617	−1778.330374	−1778.190546	3.805
cc-pVQZ	−0.499946	−459.693052	−1778.373417	−1778.232664	3.830
cc-pV5Z	−0.499995	−459.697204	−1778.391928	−1778.250514	3.848
CBS[b]					3.844
cc-pVTZ-DKH	−0.499816	−461.081645	−1794.719333	−1794.572838	3.986
cc-pVQZ-DKH	−0.499952	−461.103620	−1794.763415	−1794.615809	4.017
cc-pV5Z-DKH	−0.500001	−461.110369	−1794.782236	−1794.633870	4.037
CBS[b]					4.035
cc-pwCVTZ		−459.949894	−1778.771514	−1778.630653	3.833
cc-pwCVQZ		−460.019850	−1778.842544	−1778.700726	3.859
cc-pwCV5Z		−460.045346	−1778.873898	−1778.731406	3.877
CBS[b]					3.874
cc-pwCVTZ-DKH			−1795.163389	−1795.015801	4.016
cc-pwCVQZ-DKH			−1795.234823	−1795.086085	4.047
cc-pwCV5Z-DKH			−1795.266213	−1795.116703	4.068
CBS[b]					4.065
expt.					4.054[c]

[a] See text for the definition of the basis set families used. [b] For complete basis set limit, see text. [c] Averaged over M_J values, see ref 14.

TABLE 2: BSSE-Corrected Energies E (E_h), Dissociation Energies D_e (kcal/mol), Bond Lengths r_e (Å) along with Dipole Moments μ (Debye) for the X $^2\Sigma^+$ States of ZnH and ZnCl at the RCCSD(T) Level of Theory

basis set	ZnH (X $^2\Sigma^+$)					ZnCl (X $^2\Sigma^+$)				
	E	$D_e{}^a$	$D_e{}^b$	r_e	μ^c	E	$D_e{}^a$	$D_e{}^b$	r_e	μ^c
cc-pVTZ	−1778.865100	21.91	109.65	1.6048	0.589	−2238.077760	47.55	135.29	2.1542	2.786
cc-pVQZ	−1778.909407	22.62	110.94	1.6007	0.588	−2238.148108	51.23	139.55	2.1500	2.835
cc-pV5Z	−1778.928354	22.86	111.60	1.6001	0.590	−2238.173107	52.70	141.43	2.1480	2.814
CBS		23.03	111.69	1.5983			53.38	142.03	2.1476	
cc-pVTZ-DKH	−1795.251864	20.53	112.46	1.5919		−2255.871934	44.53	136.45	2.1424	
cc-pVQZ-DKH	−1795.297197	21.23	113.85	1.5881		−2255.943767	48.15	140.77	2.1349	
cc-pV5Z-DKH	−1795.316438	21.46	114.56	1.5875		−2255.971627	49.59	142.69	2.1337	
CBS		21.64	114.66	1.5859			50.26	143.28	2.1305	
cc-pwCVTZ	−1779.305599	21.51	109.90	1.6061		−2238.796927	47.39	135.78	2.1556	
cc-pwCVQZ	−1799.377844	22.19	111.18	1.6023		−2238.943639	50.98	139.97	2.1453	
cc-pwCV5Z	−1779.409618	22.42	111.83	1.6017		−2239.002631	52.33	141.74	2.1430	
CBS		22.59	111.92	1.6001			53.07	142.41	2.1393	
$\Delta_{SO}{}^d$		0.00	−0.61				−0.47	−1.08		
best value[e]		21.2	114.3	1.588	0.59		49.5	142.6	2.122	2.81
CISD[f]	−1778.63062	22.6		1.587	0.723					
CPF[g]	−1778.65976	22.6		1.609	0.579					
MCPF[h]	−1778.66038	22.4		1.608	0.588					
CIPSI+CPP[i]		18.9		1.6050						
MP2[j]				1.572						
B3LYP[k]				1.622						
B3LYP[l]						−2239.594160			2.197	
MP2[m]						−2237.761140			2.137	
QCISD(T)[n]						−2237.840968	46.7		2.156°	2.782°
CISDSC[p]							41.6		2.169	
expt.		21.88(0.46)[q]		1.5949[r]			55.3(1.9)[s]				
							53.6[t]			
							49.0[u]			

[a] Binding energy with respect to adiabatic fragments Zn(^{1}S) + H(^{2}S)/Cl(^{2}P). [b] Binding energy with respect to diabatic fragments Zn(^{3}P) + H(^{2}S)/Cl(^{2}P). [c] Dipole moments calculated with the finite field method. [d] Spin−orbit coupling correction from atomic fragments. [e] See text for details. [f] Configuration interaction (CI) singles and doubles, ref 21. [g] Coupled-pair functional, ref 21. [h] Modified coupled-pair functional, ref 21. [i] Configuration interaction + semiempirical core polarization potential, ref 22. [j] Møller−Plesset second-order perturbation theory with a 6-311+G(2df) basis, ref 23. [k] Density functional theory with a 6-311++G(3df,3pd) basis, ref 24. [l] 6-311++G(d,f) basis, ref 25. [m] 6-311++G(d,f) basis, ref 26. [n] Quadratic CI with inclusion of perturbative triple excitations, 6-311++G(2d,2f) basis, ref 25. [o] At the QCISD/6-311++G(d,f) level. [p] Size-consistent CI (= CI + Pople correction) with pseudopotentials, ref 26. [q] $D_e = D_0 + \omega_e/2 - \omega_e\chi_e/4$, refs 15 and 16. [r] Reference 15. [s] D_e = thermochemical D_0 value, ref 17 + zero-point vibrational energy, ref 15. [t] D_e = thermochemical D_0 value, refs 18 and 19 + zero-point vibrational energy, ref 15. [u] Chemiluminescence in Na/ZnCl$_2$ flames, refs 15 and 20.

(−0.0083 Å) effects. Previous theoretical values at lower computational levels range from 2.14 to 2.20 Å (Table 2). Our r_e value of 2.122 Å should be the most reliable in the literature, since to the best of our knowledge no experimental value exists for ZnCl (X $^2\Sigma^+$). Finally, the predicted dipole moment is close to 2.81 D, significantly higher than in the "isovalent" ZnH (vide supra).

3.b. HZnCl. We can now envisage the formation of HZnCl, by either H(^{2}S) + ZnCl (X $^2\Sigma^+$) or HZn (X $^2\Sigma^+$) + Cl(^{3}P). In either case, the following vbL picture obtains
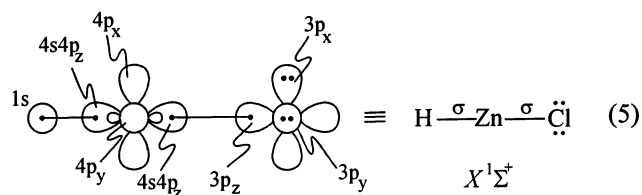

$$H \overset{\sigma}{-} Zn \overset{\sigma}{-} \ddot{\underset{..}{Cl}} \quad (5)$$

$$X^1\Sigma^+$$

10902 *J. Phys. Chem. A, Vol. 110, No. 37, 2006*

Kerkines et al.

TABLE 3: BSSE-Corrected Total Energies E (E_h), Dissociation Energies D_e (kcal/mol), Atomization Energies AE (kcal/mol), Bond Lengths r_e (Å), and Dipole Moments μ (Debye) of the X $^1\Sigma^+$ State of HZnCl at the RCCSD(T) Level of Theory

basis set	E	D_e (H−ZnCl)[a]	D_e (HZn−Cl)[b]	AE[c]	AE[d]	r_e (H−ZnCl)	r_e (HZn−Cl)	μ
cc-pVTZ	−2238.703532	79.04	104.68	126.59	214.33	1.5216	2.1114	1.763
cc-pVQZ	−2238.776051	80.32	108.93	131.55	219.87	1.5187	2.1018	1.789
cc-pV5Z	−2238.801993	80.88	110.72	133.58	222.31	1.5178	2.0965	1.774
CBS		81.06	111.40	134.44	223.09	1.5170	2.0962	
cc-pVTZ-DKH	−2256.499473	80.15	104.14	124.67	216.60	1.5047	2.0988	
cc-pVQZ-DKH	−2256.573518	81.45	108.37	129.60	222.22	1.5016	2.0886	
cc-pV5Z-DKH	−2256.602354	82.03	110.16	131.62	224.72	1.5006	2.0832	
CBS		82.21	110.83	132.47	225.49	1.4998	2.0827	
cc-pwCVTZ	−2239.422579	78.97	104.85	126.36	214.75	1.5206	2.1076	
Δ_{SO}[e]		0.00	−0.47	−0.47	−1.08			
best value[f]		82.1	110.5	131.8	224.8	1.499	2.079	1.78
RHF[g]						1.554	2.140	
B3LYP[h]						1.519	2.114	
B3LYP[i]						1.156	2.151	
MP2[h]						1.497	2.082	
MP4(SDQ)[j]						1.511	2.094	
QCISD[h]						1.519	2.102	
expt.[k]						1.70480	2.08346	
						1.75796		

[a] Binding energy with respect to H(^{2}S) + ZnCl(X $^2\Sigma^+$). [b] Binding energy with respect to Cl(^{2}P) + ZnH(X $^2\Sigma^+$). [c] Atomization energy with respect to adiabatic fragments Zn(^{1}S) + H(^{2}S) + Cl(^{2}P). [d] Atomization energy with respect to diabatic fragments Zn(^{3}P) + H(^{2}S) + Cl(^{2}P). [e] Spin−orbit correction from atomic fragments, ref 14. [f] See text for details. [g] Restricted Hartree−Fock/6-311++G(3df,3pd), ref 2. [h] 6-311++G(3df,3pd) basis, ref 2. [i] CEP-31G basis, ref 1. [j] Fourth-order Møller−Plesset perturbation theory with single, double, and quadruple excitations/6-311++G(3df,3pd) basis, ref 2. [k] Reference 2.

TABLE 4: Calculated and Experimental Harmonic Frequencies (cm^{-1}) and Zero-Point Energies (ZPE, cm^{-1}) for Different Isotopomers of HZnCl (X $^1\Sigma^+$) at the RCCSD(T)/cc-pVTZ Level of Theory[a]

isotopomer	natural abundance[b]	$\omega_1(\sigma^+)$	$\omega_2(\pi)$	$\omega_3(\sigma^+)$	ZPE (cm^{-1})
H^{64}Zn^{35}Cl	36.8%	2008.2 (2023.1)[c] (2036.8)[d]	421.2 (458.8)[c]	431.7 (424.7)[c]	1641 (1638[e]/1682[f])
H^{66}Zn^{35}Cl	21.1%	2007.7	420.9	429.4 (422.6)[c]	1639
H^{68}Zn^{35}Cl	14.2%	2007.2	420.6	427.3 (420.5)[c]	1638
H^{64}Zn^{37}Cl	11.8%	2008.2	421.0	424.0 (417.3)[c]	1637
H^{66}Zn^{37}Cl	6.8%	2007.7	420.7	421.7 (415.1)[c]	1635
H^{68}Zn^{37}Cl	4.6%	2007.2	419.6	421.3 (412.8)[c]	1634
D^{64}Zn^{35}Cl	<0.1%	1432.0 (1443.0)[c]	306.4 (330.3)[c]	430.3 (424.0)[c]	1238
D^{66}Zn^{35}Cl	<0.1%	1431.3	306.0	428.2 (421.9)[c]	1236
D^{68}Zn^{35}Cl	<0.1%	1430.7	305.6	426.1 (420.0)[c]	1234
D^{64}Zn^{37}Cl	<0.1%	1432.0	306.2	422.7 (416.3)[c]	1234
D^{66}Zn^{37}Cl	<0.1%	1431.3	305.8	420.5 (413.9)[c]	1232
D^{68}Zn^{37}Cl	<0.1%	1430.7	305.4	418.3	1230

[a] Experimental values from literature in parentheses. [b] Values calculated according to isotopic natural abundances for atoms, ref 28. [c] Harmonized matrix-isolated IR spectrum frequencies, ref 1. [d] Gas-phase IR emission spectrum observed frequency (ref 2), harmonized using an anharmonicity constant from ref 1. [e] Harmonic ZPE. [f] Observed ZPE including anharmonicities.

interpreting at the same time the observed linearity of HZnCl in its ground state.

Table 3 contains our results for HZnCl (X $^1\Sigma^+$) at the RCCSD(T) level of theory. As indicated by the T_1 diagnostic[27] of 0.015, there are no significant nondynamical correlation contributions, thus a single reference methodology can accurately describe the HZnCl system around equilibrium. Due to the size of the molecular problem, core/valence calculations were performed only with the cc-pwCVTZ basis, however, this basis set is adequate to extract a fairly accurate estimate for core/valence effects as shown from the ZnH and ZnCl results in Table 2. Our best optimized bond distances including core/valence and DKH relativistic effects are H−ZnCl = 1.499 Å and HZn−Cl = 2.079 Å. The latter value is in very good agreement with the experimental values of Yu et al., r_{HZn-Cl} = 2.079−2.088 and 2.08346 Å, obtained with the use of the Kraitchman equation.[2] However, the Zn−H bond length is predicted to be much smaller from the experimental estimates of 1.596−1.789 and 1.70480 and 1.75796 Å derived from the Kraitchman equation.[2] This is in accordance with the DFT calculations of Yu et al., who predicted a bond length close to 1.50−1.52 Å.[2] At this point, we should mention that these

authors have considered their DFT value more reliable than their experimental r_e for the H−ZnCl bond and indeed the present results corroborate with that.[2] In addition, gas-phase IR emission spectra has recently shown that the Zn−H bond length in the linear ZnH$_2$ molecule is 1.524 Å,[29,30] a number much closer to the 1.50−1.52 Å range than to the 1.70−1.75 Å one.

What is interesting again is the effect of one-electron relativistic effects on the bond lengths. Comparison of CBS bond length values indicates that relativistic effects reduce the bond lengths by 0.013−0.017 Å, while inclusion of the $(3s^23p^6)_{Zn}$ and $(2s^22p^6)_{Cl}$ electrons has a similar but smaller effect (0.001−0.004 Å); see Table 3.

The H−ZnCl and HZn−Cl CBS nonrelativistic extrapolated binding energies are 81.06 and 111.40 kcal/mol. These values are changed upon inclusion of relativity by +1.15 and −0.57 kcal/mol, whereas core/valence correlation exhibits a much smaller effect (Table 3). In summary, our best estimates for the H−ZnCl and HZn−Cl binding energies are 82.1 and 110.5 kcal/mol, thus both bonds have become about 32 kcal/mol weaker in comparison with the bonds in the diatomics ZnH and ZnCl, 114.3 and 142.6 kcal/mol with respect to Zn(^{3}P) + H(^{2}S)/Cl(^{2}P); see Table 2.

Structure and Energetics of Gaseous HZnCl

J. Phys. Chem. A, Vol. 110, No. 37, 2006 **10903**

Table 4 contains calculated and experimental harmonic frequencies for a variety of HZnCl isotopomers. At the RCCSD(T)/cc-pVTZ level of theory, the ω_1 (H—ZnCl stretching) frequency of the most abundant $H^{64}Zn^{35}Cl$ isotopomer is found to be 2008.2 cm^{-1}, in good agreement with the matrix value[1] of 2023.1 and the gas-phase value[2] of 2036.8 cm^{-1}. It is noted that the latter value is a "harmonized" value after correcting the experimentally observed vibration with an anharmonicity constant χ_i from ref 1. Similar arguments hold for the deuterated isotopomer which has also been observed experimentally in the matrix.[1] The calculated ω_1 frequency for $D^{68}Zn^{35}Cl$ is 1432.0 cm^{-1}, only 11 cm^{-1} smaller than the harmonized matrix value of 1443.0 cm^{-1}. In general, very good agreement is observed with experiment (where available) in the case of ω_2 and ω_3 frequencies taking into account the complexity of the problem.

4. Concluding Remarks

To pinpoint an accurate number on the problematic H—ZnCl bond length, an exhaustive theoretical study was undertaken in the present work. A large discrepancy was found between theory and experiment. We are confident that our extrapolated H—ZnCl r_e value of 1.499 Å is accurate, and we agree that the spectrum of DZnCl needs to be measured to confirm this result and give the final "verdict". Apart from the geometry, individual bond strengths, total atomization energies, and dipole moments were also calculated at various levels of theory. A similar approach was used in the ground-state ZnH and ZnCl diatomics, knowledge of which is crucial for a clear understanding of the bonding characteristics in HZnCl. In particular, for ZnCl ($X^2\Sigma^+$) where no experimental r_e value exists, our "best" r_e value is expected to be a fairly reliable estimate. Relativistic effects obtained with the use of the second-order Douglas—Kroll—Hess approximation were found to be influential in dissociation and atomization energies.

Finally, the convergence properties of the new Balabanov—Peterson basis sets for Zn were monitored. Due to the size and nature of the specific problem, severe BSSE issues were observed which initially prevented any extrapolation attempt. In certain cases, the oscillatory behavior of, for instance, the Zn—H binding energies in ZnH ($X^2\Sigma^+$) as the basis set increased was an indicator of BSSE presence. However, in other cases, the basis set cardinal number was not so high (even up to the 5Z level) to let this oscillatory behavior appear. Instead, BSSE revealed itself only after these initial extrapolations, with the CBS limits showing unexpected discrepancies. In the particular cases of ZnCl and HZnCl, a significant source for these discrepancies was the use of the plain cc-pVnZ sets for Cl. Indeed, convergence issues for 2nd main row elements in conjunction with cc-pVnZ sets have been carefully studied by Dunning et al. and have been corrected with the establishment of the cc-pV(n+d)Z basis set family.[31] In the present work, however, it was shown that a counterpoise BSSE correction was enough to make all such problems disappear and let smooth convergence be achieved.

References and Notes

(1) Macrae, V. A.; Green, J. C.; Greene, T. M.; Downs, A. J. *J. Phys. Chem. A* **2004**, *108*, 9500.

(2) Yu, S.; Shayesteh, A.; Fu, D.; Bernath, P. F. *J. Phys. Chem. A* **2005**, *109*, 4092.

(3) Stevens, W. J.; Krauss, M.; Basch, H.; Jasien, P. G. *Can. J. Chem.* **1992**, *70*, 612.

(4) Gordy, W.; Cook, R. L. *Microwave Molecular Spectra*; Interscience Publishers: New York, 1970.

(5) Balabanov, N. B.; Peterson, K. A. *J. Chem. Phys.* **2005**, *123*, 064107.

(6) (a) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479. (b) Bartlett, R. J.; Watts, J. D.; Kucharski, S. A.; Noga, J. *Chem. Phys. Lett.* **1990**, *165*, 513. (c) Bartlett, R. J.; Watts, J. D.; Kucharski, S. A.; Noga, J. *Chem. Phys. Lett.* **1990**, *167*, 609E.

(7) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007.

(8) Peterson, K. A.; Dunning, T. H., Jr. *J. Chem. Phys.* **2002**, *117*, 10548.

(9) (a) Douglas, M.; Kroll, N. M. *Ann. Phys. (N.Y.)* **1974**, *82*, 89; (b) Hess, B. A. *Phys. Rev. A* **1985**, *32*, 756; (c) Hess, B. A. *Phys. Rev. A* **1986**, *33*, 3742.

(10) de Jong, W. A.; Harrison, R. J.; Dixon, D. A. *J. Chem. Phys.* **2001**, *114*, 48.

(11) Peterson, K. A.; Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1994**, *100*, 7410.

(12) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.

(13) MOLPRO, a package of ab initio programs designed by Werner, H.-J. and Knowles, P. J. version 2002.6, Amos, R. D.; Bernhardsson, A.; Berning, A.; Celani, P.; Cooper, D. L.; Deegan, M. J. O.; Dobbyn, A. J.; Eckert, F.; Hampel, C.; Hetzer, G.; Knowles, P. J.; Korona, T.; Lindh, R.; Lloyd, A. W.; McNicholas, S. J.; Manby, F. R.; Meyer, W.; Mura, M. E.; Nicklass, A.; Palmieri, P.; Pitzer, R.; Rauhut, G.; Schütz, M.; Schumann, U.; Stoll, H.; Stone, A. J.; Tarroni, R.; Thorsteinsson, T.; Werner, H.-J.

(14) Ralchenko, Y.; Jou, F.-C.; Kelleher, D. E.; Kramida, A. E.; Musgrove, A.; Reader, J.; Wiese, W. L.; Olsen, K. *NIST Atomic Spectra Database*, version 3.0.3; http://physics.nist.gov/PhysRefData/ASD/index.html, U.S. DOC, 2005.

(15) Huber, K. P.; Herzberg, G. H. *Molecular Spectra and Molecular Structure, Vol. IV: Constants of Diatomic Molecules*; Van Nostrand Reinhold: New York, 1979.

(16) The same D_0, ω_e, and $\omega_e x_e$ values are given in Herzberg, G. H. *Molecular Spectra and Molecular Structure, Vol. I: Spectra of Diatomic Molecules*; Van Nostrand Company Inc: Princeton, NJ, 1950. A value of $D_0 = 0.845 \pm 0.020$ eV is given in Gaydon, A. G. *Dissociation Energies and Spectra of Diatomic Molecules*; Chapman and Hall Ltd.: London, 1968. Surprisingly, both D_0 values and spectroscopic parameters appear to stem from Steinvikel, G. Dissertation, Stockholm, Sweden, 1935.

(17) Hildenbrand, D. L.; Lau, K. H.; Roos, J. W. *J. Chem. Phys.* **1999**, *111*, 1337.

(18) Corbett, J. D.; Lynde, R. A. *Inorg. Chem.* **1967**, *6*, 2199.

(19) *IVTANTHERMO Database on Thermodynamic Properties of Individual Substances*; CRC Press: Boca Raton, FL, 1993.

(20) Horn, E.; Polanyi, M.; Sattler, H. *Z. Phys. Chem. B* **1932**, *17*, 220.

(21) Chong, D. P.; Langhoff, S. R.; Bauschlicher, C. W.; Walch, S. P.; Partridge, H. *J. Chem. Phys.* **1986**, *85*, 2850.

(22) Jamorski, Ch.; Dargelos, A.; Teichteil, Ch.; Daudey, J. P. *J. Chem. Phys.* **1994**, *100*, 917.

(23) Brownridge, S.; Grein, F.; Tatchen, J.; Kleinschmidt, M.; Marian, C. M. *J. Chem. Phys.* **2003**, *118*, 9552.

(24) Wang, X.; Andrews, L. *J. Phys. Chem. A* **2004**, *108*, 11006.

(25) Boldyrev, A. I.; Simons, J. *Mol. Phys.* **1997**, *92*, 365.

(26) Bowmaker, G. A.; Schwerdtfeger, P. *J. Mol. Struct. (THEOCHEM)* **1990**, *205*, 295.

(27) Lee, T. J.; Taylor, P. R. *Int. J. Quantum Chem.: Quantum Chem. Symp.* **1989**, *23*, 199.

(28) Krane, K. S. *Introductory Nuclear Physics*; J. Wiley and Sons: New York, 1988.

(29) Shayesteh, A.; Appadoo, D. R. T.; Gordon, I. E.; Bernath, P. F. *J. Am. Chem. Soc.* **2004**, *126*, 14356.

(30) Shayesteh, A.; Appadoo, D. R. T.; Gordon, I. E.; Bernath, P. F. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3132.

(31) Dunning, T. H., Jr.; Peterson, K. A.; Wilson, A. K. *J. Chem. Phys.* **2001**, *114*, 9244.