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Accurate Indium Bond Energies

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InX_n atomization energies are computed for $n = 1-3$ and X = H, Cl, and CH_3. The geometries and frequencies are determined using density functional theory. The atomization energies are computed at the coupled cluster level of theory. The complete basis set limit is obtained by extrapolation. The scalar relativistic effect is computed using the Douglas−Kroll approach. While the heats of formation for InH, InCl, and $InCl_3$ are in good agreement with experiment, the current results show that the experimental value for $In(CH_3)_3$ must be wrong.

I. Introduction

Indium compounds are used in chemical vapor deposition (CVD) processes. At high temperatures these compounds can begin to decompose, and this needs to be accounted for in any accurate modeling of the CVD processes. While there have been very limited experimental studies of thermochemisty recently, ab initio calculations have reached the point where it is routinely possible to compute highly accurate bond energies for systems composed of first and second row atoms. We have recently found[1,2] that it is possible to extend these studies to systems containing third and fourth row atoms, if one accounts for the scalar relativistic effects. In this paper we report on accurate bond energies for several indium-containing compounds. The InCl and $InCl_3$ atomization energies have been published[2] previously as a test of the methods used in this work and are given in this work for completeness.

There is limited previous theoretical work on these systems. Balasubramanian and co-workers[3,4] have studied InH_n, for $n = 1-3$, and InCl, reporting both geometries and binding energies. Stoll, Dolg, Schwerdtfeger, and co-workers[5,6] have studied InCl and $InCl_3$ using various effective core potentials. There is also limited experimental work on these systems. Gurvich et al.[7] report values for $InCl_n$, for $n = 1-3$, and for InH. However, we should note that the value for $InCl_2$ is only an estimate. Price and co-workers[8] report a value for $In(CH_3)_3$, but recent experiments by McDaniel and Allendorf[9] suggest that this value is uncertain because of reactions occurring on the reactor surfaces.

II. Methods

The geometries are optimized using the hybrid[10] B3LYP[11] and BP86[12,13] functionals. The 6-31+G* basis sets[l4] are used for H, C, and Cl, and the Los Alamos effective core potential[15] (ECP) and associated double-zeta basis set (denoted LANL2DZ in *Gaussian 94*) are used for indium. The harmonic frequencies confirm that the stationary points correspond to minima and are used to compute the zero-point energies.

The energetics are computed using the restricted coupled cluster singles and doubles approach[16,17] including the effect of connected triples determined using perturbation theory,[18,19] RCCSD(T). In the RCCSD(T) calculations, the In 4d, 5s, and 5p electrons, the chlorine 3s and 3p electrons, the carbon 2s and 2p electrons, and the hydrogen 1s electrons are correlated. The H and C basis sets are the correlation consistent valence polarized (cc-pV) sets developed by Dunning co-workers.[20−23] For C1, the augmented (aug) cc-pV basis sets[22,23] are used. For In, we use our recently developed[2] cc-pV sets, where the polarization functions are determined for 13 valence electrons. The triple zeta (TZ), quadruple zeta (QZ), and quintuple zeta (5Z) sets are used. To improve the accuracy of the CCSD(T) results, we extrapolate to the complete basis set (CBS) limit using the two-point[24,25] and three-point[24] schemes.

There are no first-order spin-orbit effects for InX and InX_3 because they have closed shell ground states; therefore, we account only for the atomic spin-orbit effects, using the tabulation of Moore.[26] Since the InX_2 systems are nonlinear, we expect very small spin-orbit effects, and therefore we only account for the atomic effects in these systems as well. The scalar relativistic effects are computed as the differences between results obtained using the nonrelativistic and Douglas−Kroll (DK) approaches.[27] More specifically, the systems are studied at the modified coupled pair functional[28] (MCPF) level of theory using the cc-pVTZ basis set (aug-cc-pVTZ for Cl). Note that the contraction coefficients used in the molecular DK calculations are taken from DK atomic self-consistent-field (SCF) calculation.

For InCl, some additional calibration calculations are performed: (1) the effect of inner-shell (Cl 2s and 2p and In 4s and 4p) correlation on the dissociation energy is account for, (2) the scalar relativistic effect is computed at the CCSD(T) level, (3) the effect of basis set contraction on the scalar relativistic effect is computed, and (4) the RCCSD(T) approach is compared to the restricted open-shell Hartree−Fock (ROHF) CCSD(T) approach.[l9,29] The calculations that test in importance of core−core and core−valence (CV) correlation use a modified version of the aug-cc-pVTZ basis sets; for In, the d contraction is made more flexible by uncontracting two more functions, i.e., eight instead of ten d primitives are used to describe the 3d and 4d contracted functions and a tight f (8.38) function is added. For Cl, the inner eight s primitives are contracted to two functions and the inner 4 p primitives are contracted to one function. The remaining s and p primitives are uncontracted. Two tight d (9.41 and 3.14) functions and a tight f (2.12) function are added.

The DFT calculations are performed using *Gaussian 94*;[30] the ROHF-CCSD(T) calculations are performed using MOLCAS4;[31] all of the remaining CCSD(T) calculations are performed using Molpro;[32] and the MCPF calculations are per-

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TABLE 1: Summary of InCl Spectroscopic Constants

	r_e(Å)	D_e(kcal/mol)	ω_e (cm^{-1})
TZ MCPF	2.423	102.87	318
TZ^a MCPF(DK)	2.425	101.62	318
TZ CCSD(T)	2.423	105.15	317
QZ CCSD(T)	2.412	107.70	318
5Z CCSD(T)	2.406	108.69	319
6-31+G* BP86	2.432		284
6-31+G* B3LYP	2.426		284
Expt[35]	2.401		317

[a] The contraction is taken from DK SCF calculations.

formed using Molecule-Sweden.[33] The DK integrals are computed using a modified version of the program written by Hess.

The heat capacity, entropy, and temperature dependence of the heat of formation are computed for 300 to 4000 K using a rigid rotor/harmonic oscillator approximation. The DFT frequencies are used in these calculations. These results are fit in two temperature ranges, 300−1000 K and 1000−4000 K using the Chemkin[34] fitting program and following their constrained three step procedure.

III. Results and Discussion

The geometries and harmonic frequencies computed using the BP86 and B3LYP functionals are very similar. The InH_n and $InCl_n$ species, for $n = 1-3$, have $C_{\infty v}$, C_{2v}, and D_{3h} symmetry, respectively. For InX_2, the XInX angle is about 118 degrees. The heavy atoms in $In(CH_3)_n$ have the same symmetry as the analogous InH_n or $InCl_n$ system, but the hydrogen atoms in $In(CH_3)_n$ lower the symmetry. For $In(CH_3)_2$ and $In(CH_3)_3$ there are very small deformations of the CH_3 groups, so that $In(CH_3)_2$ has C_2 instead of C_{2v} and $In(CH_3)_3$ has C_s instead of C_{3v} symmetry.

Our InH_n geometries are similar to those Balasubramanian and Tao;[3] consider InH_2, for example, where their SOCI In−H bond length and HInH angle are 1.782 Å and 119.7 degrees, respectively, compared with our BP86(B3LYP) results of 1.789(1.772) Å and 118.0(118.0) degrees. For InCl, Leininger et al.[6] report CCSD(28) bond lengths ranging from 2.422 to 2.430 Å, which are consistent with our BP86 value of 2.432 and our B3LYP value of 2.426 Å, all of which are somewhat longer than the experimental value[35] of 2.401 Å. On the other hand, the value of Balasubramanian, Tao, and Liao[4] (2.37 Å) is shorter than experiment.

Our InCl results are summarized in Table 1. The nonrelativistic and DK MCPF results show a very small scalar relativistic effect on r_e and ω_e. The dissociation energy is slightly reduced because of scalar relativistic effects; note that a detailed comparison of the computed and experimental binding energies is given below. The MCPF and CCSD(T) results in the TZ basis sets are in good agreement for r_e and ω_e. The CCSD(T) has a larger binding energy, as expected. As the basis set is improved, the bond length shortens and the dissociation energy and frequency increase. The agreement with experiment[35] for r_e and ω_e is very good. The BP86 and B3LYP r_e values are slightly longer than the CCSD(T) values using the TZ basis set, and therefore in reasonable agreement with experiment. Unlike the CCSD(T) results, the BP86 and B3LYP ω_e values are about 10% smaller than experiment. Overall, the DFT results are in reasonable agreement with experiment, and their computational cost allows them to be applied easily to the largest systems considered. Thus, the DFT approaches are used to determine the geometry and zero-point energies.

Before continuing to the larger systems, we report on some additional calibration calculations performed for InCl. Ideally one would compute the scalar relativistic effect using the same uncontracted basis set[36] for the nonrelativistic and DK calculation, but this would lead to very large calculations for the largest systems. However, it is possible to run InCl using an uncontracted basis set to check the effect of using two different contractions, and, at the MCPF level, we find that uncontracting the basis set increases the relativistic effect by 0.028 kcal/mol. Thus, using separate contractions for the nonrelativistic and DK calculations does not lead to any significant error. Using the ROHF-CCSD(T) approach, in conjunction with the DK approximation, reduces the scalar relativistic effect by 0.12 kcal/mol relative to the MCPF approach. This is not surprising since electron correlation reduces the size of the effect and the CCSD(T) is a higher level approach. However, we note that using the ROHF-CCSD(T) approach decreases the dissociation energy by 0.23 kcal/mol relative to the RCCSD(T) approach. Thus the choice of the CCSD(T) approach, i.e., ROHF−CCSD(T) vs RCCSD(T), changes the atomization energy by more than using the MCPF rather than the more computationally demanding CCSD(T) approach to compute the scalar relativistic effect. Finally, we note that including In 4s and 4p and Cl 2s and 2p correlation increases the dissociation energy by 0.18 kcal/mol without accounting for basis set superposition error (BSSE) and decreases it by 0.07 kcal/mol if a BSSE correction is included. On the basis of these calibration calculations, we conclude that our standard approach does not introduce a significant error into the calculation of the dissociation energy.

TABLE 2: Summary of $InCl_n$ Atomization Energies, in kcal/mol

	InCl	$InCl_2$	$InCl_3$
CCSD(T) TZ	105.156	153.041	242.800
CCSD(T) QZ	107.716	158.047	250.719
CCSD(T) 5Z	108.684	159.893	
*n*3(TQ)^a	109.60	161.70	256.50
*n*3(Q5)	109.72	161.83	
*n*4(TQ)	109.21	160.94	255.29
*n*4(Q5)	109.49	161.39	
*n*4*n*6	109.59	161.55	
variable α	109.75	161.80	
CCSD(T) CBS	109.59	161.55	256.50
MCPF TZ	102.873	148.854	236.047
MCPF(DK)TZ	101.628	139.221	220.922
scalar rel	−1.245	−9.633	−15.125
spin orbit (Moore[26])	−5.057	−5.897	−6.736
zero-point energy	−0.405	−0.985	−1.893
best estimate	102.81	145.04	232.74

[a] The extrapolation methods are discussed in the text, and the basis used in the extrapolation is given in parentheses. For example, *n*3(TQ) means that the TZ and QZ basis are used in the two point n^{-3} extrapolation. [b] The CCSD(T) value is -0.455 kcal/mol.

Using the BP86 geometries, the $InCl_n$ atomization energies are computed and these results are summarized in Table 2. For InCl and $InCl_2$, it is possible to use the TZ, QZ, and 5Z basis sets, while for $InCl_3$ only the TZ and QZ sets are used because of computational cost. The results are extrapolated to the CBS limit using several approaches. On the basis of experience, we believe that the three point $n^{-4} + n^{-6}$ approach[24] (denoted *n*4*n*6 in the table) is the most reliable. The variable α approach is in reasonable agreement with the *n*4*n*6 approach. Of the two-point approaches using only the TZ and QZ basis sets, the n^{-3} approach[25] (denoted *n*3 in the tables) agrees better with the *n*4*n*6 approach, and, therefore, this is the approach we use to compute our $InCl_3$ CBS value.

The scalar relativistic effect is small for InCl because the bonding involves mostly the In 5p electron and relativity affects mostly s electrons. Since In sp hybridizes to form more than

TABLE 3: Summary of InH_n Atomization Energies,[a] in kcal/mol

	InH	InH_2	InH_3
CCSD(T) TZ	63.142	101.697	177.219
CCSD(T) QZ	64.050	103.380	179.759
CCSD(T) 5Z	64.358	103.864	180.477
CCSD(T) CBS	64.619	104.223	181.003
MCPF TZ	62.894	101.725	176.904
MCPF(DK) TZ	61.968	96.389	170.646
scalar rel	−0.926	−5.336	−6.259
spin orbit (Moore[26])	−4.217	−4.217	−4.217
ZPE(B3LYP)	−2.020	−5.439	−10.119
best estimate	57.457	89.230	160.408

[a] The B3LYP geometries are used.

one bond, the scalar relativistic grows dramatically with the number of Cl atoms. The scalar relativistic effect also increases with the ionic contribution to the bonding; consider that the electron affinity of Cl is decreased by 0.28 kcal/mol by scalar relativistic effects, while the first three In ionization potentials show scalar relativistic effects of 1.55, −18.22, and −26.28 kcal/mol, respectively. Therefore as the charge transfer from In to Cl increases with number of Cl atoms, so does the scalar relativistic effect. The spin-orbit effect is sizable, mostly because of the large In splitting. After including the zero-point energies, we obtain our best estimate for the atomization energy at 0 K. Our best D_e value for InCl (103.2 kcal/mol) is larger than that found in previous work, 96.9[4] and 98.7−100.8[6], mostly owing to our extrapolation to the CBS limit.

The InH_n results are summarized in Table 3. Since it is possible to perform the 5Z calculation for InH_3, the $n4n6$ extrapolation is used for all three systems. The scalar relativistic effect is smaller for InH_n than for $InCl_n$ because there is less charge transfer for InH_n than for $InCl_n$. Our best estimates are in good agreement with those of Balasubramanian and Tao;[3] their atomization energies, without zero-point effect, are 60, 91.5, and 161.5 kcal/mol, compared with our analogous values of 59.5, 94.7, and 170.5 kcal/mol. Our values are more reliable since we have extrapolated to the basis set limit.

The $In(CH_3)_n$ results are summarized in Table 4. The lower symmetry and additional atoms mean that the $In(CH_3)_n$ calculations are much more computationally demanding. As a result, we are forced to make some compromises. Since we are only computing the $In-CH_3$ bond energies, we performed tests where the hydrogen set is restricted to TZ regardless of the sets used for In and C, which is denoted as nZ/H(TZ); clearly TZ/H(TZ) is equivalent the TZ set. For $InCH_3$, we find that while the $n4n6$ extrapolation is essentially the same for the cc-pV and cc-pV/H(TZ) sets, the results obtained with the two-point approach using the TZ and QZ sets differ from the results obtained using the TZ and QZ/H(TZ) basis sets, and none of the two-point approaches are in good agreement with the $n4n6$ result. For $In(CH_3)_2$, we do not have the $n4n6$ results for comparison, but we note that the two-point extrapolations using the cc-pV basis sets do not agree with those using the cc-pV/H(TZ) basis sets.

For $InCH_3$, we take the $n4n6$ extrapolation using the TZ, QZ, and 5Z basis sets as our best result. If we assume that the variation between the different extrapolation approaches contains information about the basis set convergence, we can develop a method to scale the extrapolated results of the larger systems using only the TZ and QZ/H(TZ) results. With this in mind, we note that for $InCH_3$

$$n3(\mathrm{TQ}) + (n3(\mathrm{TQ}) - n4(\mathrm{TQ})) \times 0.52$$

and

$$n3(\mathrm{TQ/H(TZ)}) + (n3(\mathrm{TQ/H(TZ)}) - n4(\mathrm{TQ/H(TZ)})) \times 2.12$$

yield $In-CH_3$ bond energies in excellent agreement with the $n4n6$ result. Applying these formulae to $In(CH_3)_2$ yields 91.72 and 91.77 kcal/mol. We take the average of these two (91.75 kcal/mol) as our best value; this is 0.25 kcal/mol larger than the $n3$(TQ) value. Considering that we are breaking two $In-CH_3$ bonds and rehybridizing In, this seems consistent with the 0.11 kcal/mol difference between the $InCH_3$ $n3$(TQ) and $n4n6$ results. Given the good agreement of the results obtained with these formulae with the $n4n6$ results for $InCH_3$, and the consistency of the results obtained using the two formulae for $In(CH_3)_2$, we assume that this approach is reasonable and apply the latter formula to $In(CH_3)_3$, which yields 161.46 kcal/mol.

It is difficult to assign an uncertainty to such a scaling of the extrapolated results, but we can apply the first formula to $InCl_n$ and InH_n and compare the results to the $n4n6$ results. Using InCl to determine the scale factor for the $n3$(TQ) and $n4$(TQ) results and applying it to $InCl_2$ results yields a best estimate that differs from the $InCl_2$ $n4n6$ value by 0.12 kcal/mol. Using InH to determine the scale factor yields errors of 0.21 and 0.35 kcal/mol for InH_2 and InH_3, respectively, while using InH_2 to determine the scale factor yields an error of 0.03 kcal/mol for InH_3. Thus the results are somewhat mixed, but we suspect that the scaled $In(CH_3)_3$ value is more accurate than the $n3$(TQ/

TABLE 4: Summary of $In-(CH_3)_n$ Bond Energies,[a] in kcal/mol

	$InCH_3$		$In(CH_3)_2$		$In(CH_3)_3$
	cc-pV	cc-pV/H(TZ)	cc-pV	cc-pV/H(TZ)	cc-pV/H(TZ)
CCSD(T) TZ	56.767	56.767	87.151	87.151	154.448
CCSD(T) QZ	58.224	58.052	89.667	89.400	157.862
CCSD(T) 5Z	58.826	58.711			
$n3$(TQ)	59.29	58.99	91.50	91.04	160.35
$n3$(Q5)	59.46	59.40			
$n4$(TQ)	59.06	58.79	91.12	90.70	159.83
$n4$(Q5)	59.31	59.25			
$n4n6$	59.40	59.41			
variable α	59.60	60.09			
CCSD(T) CBS	59.40		91.75		161.46
MCPF TZ	54.527		82.755		147.490
MCPF(DK)TZ	53.166		77.096		140.279
scalar rel	−1.361		−5.659		−7.211
spin orbit (Moore[26])	−4.217		−4.217		−4.217
ZPE	−2.129		−5.711		−9.630
best estimate	51.69		76.16		140.40

[a] The B3LYP geometries are used.

TABLE 5: Computed Atomization Energies and Heats of Formation at 298 K, in kcal/mol

n	AE (0 K)	AE (298 K)	ΔH[a]	ΔH previous work
InCl				
1	102.81	103.44	−16.45	−17.2 ± 1.2[b]
2	145.04	146.16	−30.18	−48 ± 12[b]
3	232.74	234.30	−89.33	−88.4 ± 2.9[b]
InH_n				
1	57.46	58.34	51.76	51.4 ± 0.5[b]
2	89.23	91.21	71.00	
3	160.41	163.69	50.62	
$In(CH_3)_n$ [c]				
1	51.69	52.80	40.26	
2	76.16	77.96	50.16	
3	140.40	143.04	20.14	41.1[d]

[a] Computed using the following heats of formation: 52.103, 28.992, 35.06, and 58.000 kcal/mol for H, C1, CH_3, and In, respectively. [b] Gurvich et al.[7] [c] The In−CH_3 bond energies are given. [d] Price and co-workerss.[8]

H(TZ)) value, but we note that *n*3(TQ/H(TZ)) and the scaled value differ by only 1.05 kcal/mol. Thus, while we believe the scaled value is the more accurate, we must concede an error of up to 2 kcal/mol, whereas we suspect the remaining values are accurate to about 1 kcal/mol.

Our best estimates for the atomization energy of $In(CH_3)_n$ are corrected for scalar relativistic, spin-orbit, and zero-point effects. The scalar relativistic effects for $In(CH_3)_n$ are much more similar to those determined for InH_n than those for $InCl_n$, which is consistent with CH_3 not being a strong electron withdrawing group.

In Table 5 we summarize our best estimate for the atomization energy at 0 K. Using the rigid rotor/harmonic oscillator in conjunction with the DFT geometries and frequencies, these atomization energies are converted to 298 K. Since the heats of formation for H,[37] Cl,[37] In,[38] and CH_3[39] are well known, it is possible to convert our computed atomization energies to heats of formation.

Our heats of formation for InCl, $InCl_3$, and InH are in good agreement with experiment.[7] Our value for $InC1_2$ differs significantly with the estimated value of Gurvich et al.[7] Our computed value for $In(CH_3)_3$ differs by 20 kcal/mol with that given by Price and co-workers.[8] Since extrapolation increased our atomization energy by only 3.5 kcal/mol, we can rule out the older value even if our extrapolation is less accurate than assumed. Thus, our result shows that $In(CH_3)_3$ is significantly more stable than believed. We believe that our values are the most accurate and consistent set of data available for these In-containing systems.

Using our heats of formation at 298 K and the DFT frequencies and geometries, we evaluate the heat capacity, entropy, and heat of formation from 300 to 4000 K. The parameters obtained from the resulting fits can be found on the web.[40]

IV. Conclusions

The atomization energies are computed for InH_n, $InCl_n$, and $In(CH_3)_n$. The CCSD(T) results are extrapolated to the complete basis set limit. The spin-orbit and scalar relativistic effects are accounted for, as are the zero-point energies. These should be the most accurate values for these In-containing compounds to date. The atomization energies are converted into heat of formation. The heat capacity, entropy, and heat of formation are determined for 300 to 4000 K. The parameters obtained from the resulting fits can be found on the web.[40]

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