

A theoretical treatment of the $\tilde{A}^2\Sigma^+$ state of the Ar–HS/Ar–SH van der Waals complex

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Phys. Chem. Chem. Phys., 2004, **6**, 5463 (DOI: 10.1039/b411989d). *Amendment published 10th January 2008*

We regret that in our original article¹ there was an inconsistency between the analytical expressions for the potential energy surface and the fit parameters given in Table 1 to the effect that the b^l parameters listed in the Table had the wrong sign. The error was in the manuscript rather than in the calculations and the results and interpretations are unchanged. The correct Table is reproduced below with sufficient significant figures to allow reproduction of the exact values given in the original article. We are grateful to Po-Yu Tsai for drawing our attention to this error.

Table 1: Parameters for the calculated potential energy surface. With values of R in Ångström, the resulting energies are given in mE_h

l	0	1	2	3	4
d^l	16.1709156264	2.34951521231	4.25392427563	0.422346076299	0.146633768692
b^l	2.25020256328	0.244644261570	1.05435669418	$9.31970762968 \times 10^{-2}$	$3.33828783014 \times 10^{-2}$
n	0	1	2	3	4
g_n^0	$1.37842790503 \times 10^{-2}$	$-9.25079984088 \times 10^{-3}$	$2.38831690943 \times 10^{-3}$	$-2.90457234881 \times 10^{-4}$	$1.37099005111 \times 10^{-5}$
g_n^1	$-8.11688047201 \times 10^{-3}$	$6.26407666976 \times 10^{-3}$	$-2.10537308596 \times 10^{-3}$	$3.68279542546 \times 10^{-4}$	$-2.65582087638 \times 10^{-5}$
g_n^2	$-1.83937834053 \times 10^{-2}$	$1.14417838087 \times 10^{-2}$	$-2.23456502901 \times 10^{-3}$	$1.03969006249 \times 10^{-4}$	$6.87657832840 \times 10^{-6}$
g_n^3	$7.56366250134 \times 10^{-3}$	$-3.01338093065 \times 10^{-3}$	$-2.44871725448 \times 10^{-4}$	$2.37436849132 \times 10^{-4}$	$-2.67343861081 \times 10^{-5}$
g_n^4	$1.48917295903 \times 10^{-2}$	$-1.34087560903 \times 10^{-2}$	$4.53037398632 \times 10^{-3}$	$-6.93462758582 \times 10^{-4}$	$4.12669690136 \times 10^{-5}$
g_n^5	$-9.25270769967 \times 10^{-3}$	$8.27628150319 \times 10^{-3}$	$-2.85901713451 \times 10^{-3}$	$4.60677256891 \times 10^{-4}$	$-2.95216354658 \times 10^{-5}$
g_n^6	$-4.71654245037 \times 10^{-3}$	$4.81558478703 \times 10^{-3}$	$-1.78713688995 \times 10^{-3}$	$2.85483527974 \times 10^{-4}$	$-1.65804982460 \times 10^{-5}$
g_n^7	$2.40531440670 \times 10^{-3}$	$-2.22007877412 \times 10^{-3}$	$7.38625005940 \times 10^{-4}$	$-1.02862714454 \times 10^{-4}$	$4.87119121063 \times 10^{-6}$
C_6^0	$-2.60698173047 \times 10^3$				
C_6^2	$-1.15402906122 \times 10^3$				
C_7^1	$-1.52783499100 \times 10^3$				
C_7^3	$-1.38463253216 \times 10^3$				
l	5	6	7		
d^l	-0.146657873279	$-2.57638253708 \times 10^{-2}$	$-7.58310377085 \times 10^{-3}$		

Notes and references

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1 David M. Hirst, Richard J. Doyle and Stuart R. Mackenzie, *Phys. Chem. Chem. Phys.*, 2004, **6**, 5463–5468

Accurate *ab initio* determination of spectroscopic and thermochemical properties of mono- and dichlorocarbenes

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Phys. Chem. Chem. Phys., 2005, **7**, 2881 (DOI: 10.1039/b596790a). *Amendment published 15th May 2008.*

Since the publication of our paper, the following misprints, errors, and misrepresentations of the computed results came to our attention, listed in the order of their occurrence:

(1) In the caption to Table 1 the correct level of theory used for the geometry optimization is CCSD(T)/aug-cc-pCVTZ instead of CCSD(T)/aug-cc-pCVQZ.

(2) In the last line in Table 1 the correct structural parameter is r_{HC} instead of r_{HCl} .

(3) The extrapolated CBS values reported in Table 8 were obtained by the use of the two-parameter eqn (2) and the extrapolation was performed by fitting the three available energies. For CCl_2 , in the case of the extrapolation of the MP2 correlation energy, in the formulas $(X + 1)$ has been used incorrectly instead of X . Furthermore, it is slightly preferable to use only two energies obtained with the two largest basis sets. The corrected CBS $\{\Delta\text{MP2}, \Delta\Delta E_{\text{TS}}(\text{CC})\}$ values for CCl_2 are $\{-160, -192\} \text{ cm}^{-1}$ instead of the originally reported $\{-143, -176\} \text{ cm}^{-1}$. The CBS $\{\Delta\text{MP2}, \Delta\Delta E_{\text{TS}}(\text{CC})\}$ values determined for HCCl using the best two energies are $\{-147, -164\} \text{ cm}^{-1}$ instead of the originally reported $\{-120, -146\} \text{ cm}^{-1}$. The new core correlation corrections change the computed triplet-singlet energy gap for CCl_2 and HCCl to $7029 \pm 60 \text{ cm}^{-1}$ (previously $7045 \pm 60 \text{ cm}^{-1}$) and $2152 \pm 40 \text{ cm}^{-1}$ (previously $2170 \pm 40 \text{ cm}^{-1}$), respectively.

(4) In Tables 10 and 12 the labels of the ν_2 and ν_3 modes of the \tilde{a} state of HCCl should be reversed throughout.

(5) In Section V.2, the first sentence of the second paragraph correctly reads as follows (the part printed in bold here was missing in the original text):

“The thermal correction of the enthalpy of formation of $\text{CCl}_2(\tilde{X}^1A_1)$ can be obtained as follows: $\Delta_f H_{298}^\circ - \Delta_f H_0^\circ[\text{CCl}_2(\tilde{X}^1A_1)] = \{H_{298} - H_0[\text{CCl}_2(\tilde{X}^1A_1)]\} - \{H_{298} - H_0[\text{C}_{\text{graphite}}]\} - \{H_{298} - H_0[\text{Cl}_2(\tilde{X}^1\Sigma_g^-)]\} = \{2.737\}^{90} - \{2.194\}^{90} - \{0.251\}^{79} \text{ kcal mol}^{-1} = 0.292 \text{ kcal mol}^{-1}$.”

(6) In Table 17 some of the entries have been incorrectly reported. These are replaced with the correct, boldface entries in the table below.

Term	$\text{HCl}(\tilde{X}^1\Sigma^+)$	$\text{H}_2(\tilde{X}^1\Sigma_g^-)$	$\text{CH}_2(\tilde{a}^1A_1)$	$\text{HCCl}(\tilde{X}^1A')$	$\text{CCl}_2(\tilde{X}^1A_1)$
HF	-460.1128048	-1.1336211	-38.8960759	-497.8630432	-956.8213197
$\delta\text{CCSD(T)}$	-0.2653160	-0.0409409	-0.1820034	-0.4221569	-0.6629743
δCCSDT	-0.0004920	-0.0000000	-0.0008128	-0.0012263	-0.0012634
δCCSDTQ	-0.0002651	-0.0000000	-0.0001826	-0.0006356	-0.0011468
ΔCC	-0.4096885	—	-0.0549573	-0.4644784	-0.8738988
ΔRel	-1.4057415	-0.0000105	-0.0150137	-1.4209184	-2.8269971
ΔDBOC	+0.0061455	+0.0004696	+0.0023621	+0.0078903	+0.0128108
ΔZPVE	+0.0067805	+0.0098838	+0.0164575	+0.0111644	+0.0041950
Sum	-462.1813819	-1.1642191	-39.1288680	-500.1534041	-961.1705943
$\Delta_f H_0^\circ$	-22.018±0.024	0	102.32±0.16	76.53±0.20	54.49±0.20

Finally, since it has been possible to perform larger electronic structure computations than those reported in the original article, a new focal-point analysis (FPA) of the computed results could be executed for both species.

Most importantly, all previous electronic structure computations have been repeated at new reference structures optimized at the frozen-core aug-cc-pV(Q+d)Z CCSD(T) level. The new computations utilized the aug-cc-pV(6+d)Z basis sets (585 contracted Gaussian functions for CCl_2) up to the CCSD(T) level of theory, aug-cc-pV(T+d)Z CCSDT(Q) results have been added, and all FPA computations have also been performed for the ground electronic state of Cl_2 .

Using the new electronic energies, the reactions $^1\text{CH}_2 + 2 \text{HCl} \rightarrow ^1\text{CCl}_2 + 2 \text{H}_2$ and $^1\text{CH}_2 + \text{Cl}_2 \rightarrow ^1\text{CCl}_2 + \text{H}_2$, the auxiliary data of the original article and, taking the average of the two new results, the enthalpy of formation of $^1\text{CCl}_2$ is computed to be $54.11 \text{ kcal mol}^{-1}$ at 0 K. Using the new electronic energies, the reactions $^1\text{CH}_2 + \text{HCl} \rightarrow ^1\text{HCCl} + \text{H}_2$, $^1\text{CH}_2 + \text{Cl}_2 \rightarrow ^1\text{HCCl} + \text{HCl}$, and $2 ^1\text{CH}_2 + \text{Cl}_2 \rightarrow 2 ^1\text{HCCl} + \text{H}_2$, the auxiliary data of the original article and, taking the average of the three new results, the enthalpy of formation of $^1\text{HCCl}$ is computed to be $76.14 \text{ kcal mol}^{-1}$ at 0 K. (Please contact the authors for details concerning the new FPA analysis.)

Taking into consideration an improved estimate of the enthalpy of formation of C_{gas} (as reported in G. Tasi, R. Izsák, G. Matisz, A. G. Császár, M. Kállay, B. Ruscic, and J. F. Stanton, *Chem. Phys. Chem.* 2006, **7**, 1664), the best *ab initio* estimate of the above table on the enthalpy of formation of $^1\text{CH}_2$ is increased by $0.13 \text{ kcal mol}^{-1}$ to $102.45 \text{ kcal mol}^{-1}$. The best estimates from this study of the 0 K enthalpies of formation of $^1\text{HCCl}$ and $^1\text{CCl}_2$ will be changed to 54.24 ± 0.20 and $76.27 \pm 0.20 \text{ kcal mol}^{-1}$.

These values, slightly different from the ones reported in the original publication, are considered to be the best computational estimates for the enthalpies of formation of $^1\text{CCl}_2$ and $^1\text{HCCl}$ available today.

Silver as acrolein hydrogenation catalyst: intricate effects of catalyst nature and reactant partial pressures

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Phys. Chem. Chem. Phys., 2008, **9**, 3559–3569 (DOI: 10.1039/b701011g). **Amendment published 14th August 2008**