Microsolvation of Methylmercury $[CH_3Hg(H_2O)_n]^+$

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Introduction

Mercury based compounds are among the most noxious chemical substances; methylmercury is one of the six more toxic substances for the environment [1].

- **Bioaccumulation** $\Rightarrow$ Mercury based compounds accumulate inside living organisms.
- **Biomagnification** $\Rightarrow$ Mercury based compound magnify the concentration along the chain food [2].

Living organisms are composed of $\approx$ **70%–80%** water. The biological action of different molecules is heavily influenced by their ability to interact with water in cellular and molecular environments.

The properties of methylmercury in aqueous environments have not been property described at the molecular level.

Prominent bulk properties of mercury and mercury based compound are linked to relativistic effects [3].

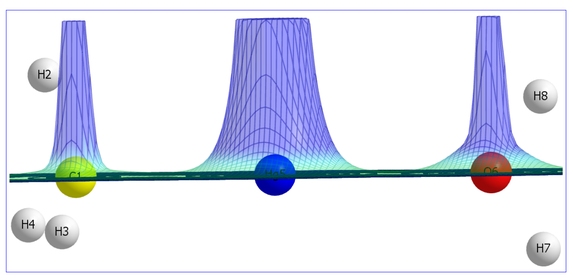
- The fluidity of mercury at ambient temperature [4].
- The availability of structure — spectroscopic correlations. NMR parameters (σ and **J**) [5].
- Condensed-phase systems [3]...

It has been recognized since the early days that NMR parameters such as nuclear shielding (σ) and **J**-coupling constants contain very useful information regarding molecular and electronic structure [6].

In this work bonding properties are analyzed within the QTAIM framework [7]. It provides a *universal definition of what constitutes bonding*.

- We gain insight from properties calculated at bond critical points (BCPs) for all kinds of interactions

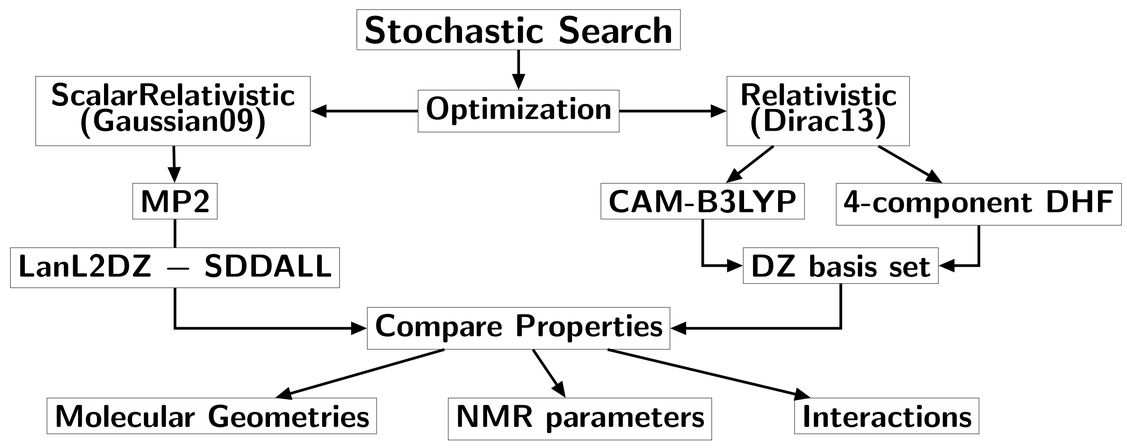
We obtained information from the properties of BCPs including electronic densities $[\rho(\mathbf{r_c})]$, its laplacian $[\nabla^2\rho(\mathbf{r_c})]$, potential $[\mathcal{V}(\mathbf{r_c})]$, kinetic $[\mathcal{G}(\mathbf{r_c})]$ and total energy densities $[\mathcal{H}(\mathbf{r_c})]$ [8,9].



$$\nabla^2\rho < \mathbf{0} \text{ Covalent interaction} \quad (1)$$
$$\nabla^2\rho > \mathbf{0} \text{ Closed shell}$$

$$\frac{|\mathcal{V}(\mathbf{r_c})|}{\mathcal{G}(\mathbf{r_c})} = \begin{cases} < \mathbf{1}; & \text{Closed shell} \\ \in [\mathbf{1},\mathbf{2}]; & \text{Intermedia level} \\ > \mathbf{2}; & \text{Covalent interaction} \end{cases} \quad (2)$$

Computational Details



Results

Table 1. Topological parameter of electronic density for Hg-O and Hg-C BCPs (Figure 1)

BCP	Structure	Oxygen	Length [Å]	$\rho(\mathbf{r_c})$	$\nabla^2\rho(\mathbf{r_c})$	$\lvert\mathcal{V}(\mathbf{r_c})\rvert/\mathcal{G}(\mathbf{r_c})$	$\mathcal{H}(\mathbf{r_c})$
Hg-O	W_1S_1	O	2.0620	0.0623	0.3479	1.0254	-0.0023
	W_2S_2	O1	2.2720	0.0599	0.3402	1.0637	-0.0044
		O2	2.7272	0.0226	0.1000	0.9818	0.0004
	W_3S_1	O	2.1359	0.0813	0.4472	1.0711	-0.0085
	W_3S_2	O1	2.8608	0.0174	0.0714	0.9069	0.0015
		O2	2.1802	0.0731	0.3988	1.0550	-0.0058
	W_3S_4	O_{equiv}	2.5077	0.0356	0.1795	1.0150	-0.0006
Hg-C	Structure		Length [Å]	$\rho(\mathbf{r_c})$	$\nabla^2\rho(\mathbf{r_c})$	$\lvert\mathcal{V}(\mathbf{r_c})\rvert/\mathcal{G}(\mathbf{r_c})$	$\mathcal{H}(\mathbf{r_c})$
	W_1S_1		2.0620	0.1285	0.0353	1.8832	-0.0642
	W_2S_2		2.1213	0.1143	0.1003	1.9450	-0.0537
	W_3S_1		2.0523	0.1343	0.0498	1.1428	-0.0114
	W_3S_2		2.1424	0.1097	0.1180	1.8642	-0.0493
	W_3S_4		2.0579	0.1319	0.0572	1.8254	-0.0655

Results (Continuation)

Basis sets used here were uncontracted and all electron. For relativistic (Rel) RPA calculations we used DHF 4-component Hamiltonian with DZ basis set and unrestricted kinetic balance (UKB). For non relativistic (NR) RPA calculations ($c\rightarrow\infty$), we used Dalton13 suite of programs and TZ basis set. Table 2 and table 4.

Table 2. NR limit of total shielding σ for W_1S_1. Figure 1.

Atom	Speed of light			
	c	5c	10c	$c\rightarrow\infty$
C	204.46	230.54	231.39	220.73
O	269.61	316.01	317.57	342.31
Hg	12228.77	8328.57	8242.61	8182.50

Table 3. Basis sets description

Level	Basis sets*		
	H	C and O	Hg
Rel	L-4s1p	L-9s4p1d	L-24s21p15d10f
	S-1s4p1d	S-1s4p1d	S-19s36p28d12f9g
NR	6s3p2d	11s6p3d2f	24s21p15d10f

*L ans S means large and small components

Table 4. Total shielding σ (C, O and Hg), interaction (C—Hg—O). Figure 1.

Atom	W_1S_1	W_2S_1	W_2S_2	W_3S_1	W_3S_2	W_3S_3	W_3S_4	W_3S_5	W_3S_6
C	204.46	123.37	113.49	182.36	161.56	264.99	196.27	269.43	161.56
O	269.61	199.15	165.22	297.14	261.75	363.12	185.96	379.85	277.10
Hg	12228.77	12535.64	12365.42	12690.92	12619.11	12456.19	12277.11	12627.09	12699.78

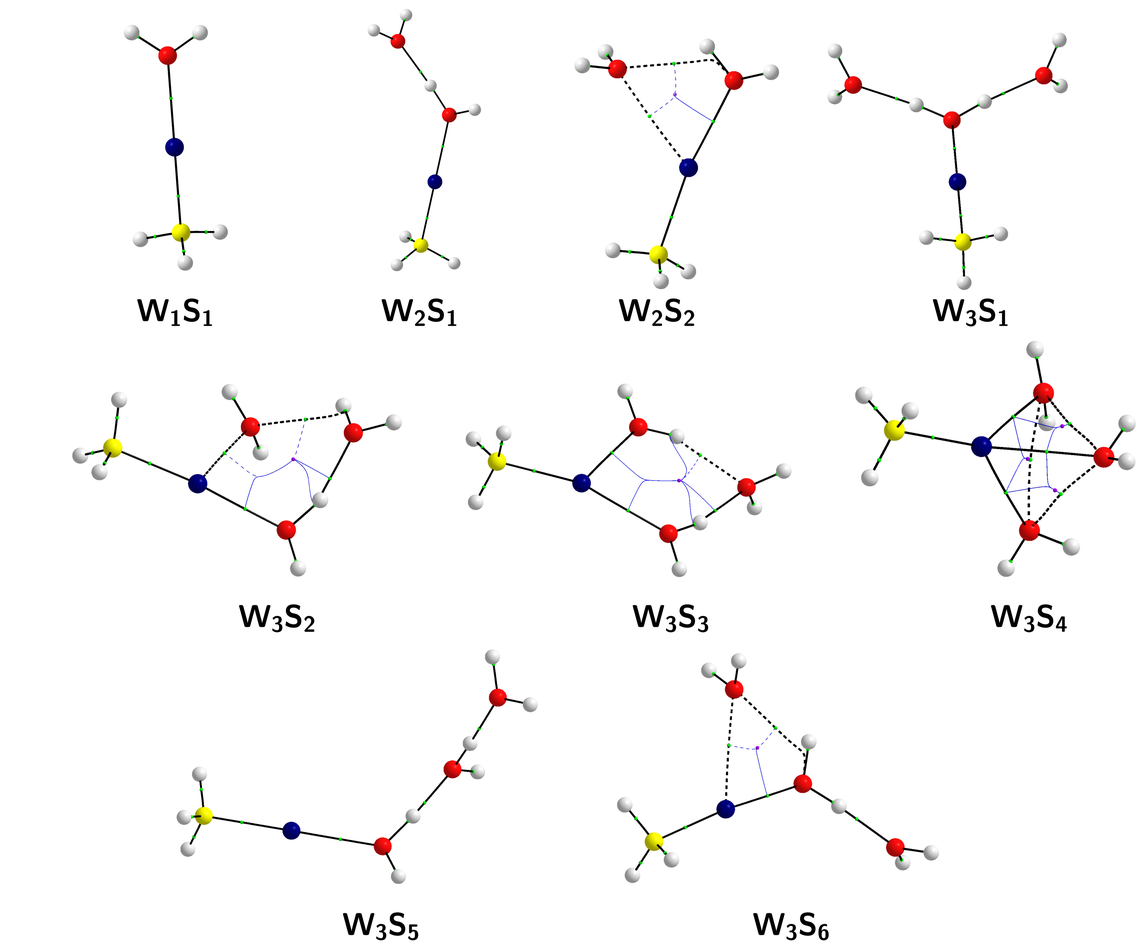


Figura 1. Equilibrium structures for $[CH_3Hg(H_2O)_n]^+$. Each molecular motif was characterized using MP2 and ECP as a true minimum within harmonic approximation. The most stable motif for each stoichiometry $\mathbf{W_1S_1}$, $\mathbf{W_2S_1}$, $\mathbf{W_3S_1}$ and $\mathbf{W_3S_3}$ were also treated using CAM—B3LYP functional in conjunction with DZ quality basis set at the 4-component level. Carbon atoms are shown in yellow, oxygen atoms in red, hydrogen atoms in white and mercury atoms in blue. BCPs are shown in green and bonding paths in black.

Remarks

- The most energetically stable conformations are those in which mercury atom is coordinated to just one water molecule
- For this particular system, the Laplacian on the electron density (eq. 1) is a better descriptor of the nature of intramolecular interactions than Espinisa's criterion (eq. 2).
- Some electronic effects that appear on the shielding of Hg, C or O are not only due to the presence of vicinal heavy atoms, some new electronic effects appear due to quantity and spatial arrangement of water molecules.
- This work suggest a new strategy of using σ and **J** to determine local geometries in the microsolvation process of methylmercury.

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