JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Article

Molecular Dynamics Computational Study of the Hg–Hg NMR Spin–Spin Coupling Constants of [Hg–Hg–Hg] in SO Solution

Jochen Autschbach, and Mariusz Sterzel

J. Am. Chem. Soc., **2007**, 129 (36), 11093-11099• DOI: 10.1021/ja073166+ • Publication Date (Web): 22 August 2007

Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

J|A|C|S
ARTICLES

Molecular Dynamics Computational Study of the ^{199}Hg−^{199}Hg NMR Spin−Spin Coupling Constants of $[Hg-Hg-Hg]^{2+}$ in SO_2 Solution

Jochen Autschbach* and Mariusz Sterzel†

Contribution from the Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14260-3000

Received May 14, 2007; E-mail: jochena@buffalo.edu

Ⓦ **This paper contains enhanced objects available on the Internet at http://pubs.acs.org/journals/jacsat.**

Abstract: The isotropic one−bond and two−bond ^{199}Hg−^{199}Hg nuclear magnetic spin−spin coupling constants (J-couplings) of $[Hg-Hg-Hg]^{2+}$ were calculated using density functional theory, the zeroth−order regular approximation (ZORA) to treat relativistic effects, and Born−Oppenheimer molecular dynamics (BOMD) including SO_2 molecules explicitly for the description of solvent effects. The final BOMD average of 150 kHz for ^1J (^{199}Hg−^{199}Hg) agrees well with the experimental spin−spin coupling of 140 kHz measured in liquid SO_2, while computations not considering explicit solvation at the quantum−mechanical level yielded one−bond coupling constants between 230 and 260 kHz. The two−bond coupling is similarly strongly affected by solvent effects. An analysis of the BOMD data shows that the effect is mainly due to close contacts between the terminal Hg atoms of $[Hg-Hg-Hg]^{2+}$ and the solvent's oxygen atoms. The results highlight the importance of solvent effects for the NMR parameter of heavy metals and demonstrate the usefulness of treating such solvent effects with the help of molecular dynamics−based averaging.

1. Introduction

Nuclear magnetic spin−spin coupling constants (J-couplings) involving ^{199}Hg nuclei have been studied for quite a long time.[1−3] These coupling constants are intriguing to researchers in the NMR field for a number of reasons. To name a few, first, coupling constants between two Hg nuclei represent the largest J-couplings known to date from experiment. Second, Hg−ligand and Hg−Hg bonds are strongly influenced by relativistic effects of the Hg 6s orbital—which is very important for J-coupling constants involving ^{199}Hg nuclei. Third, Hg spin−spin couplings are very sensitive probes for the influence from the electronic structure of a complex and from its chemical environment on Hg−ligand and Hg−Hg bonds.

Relativistic ab initio computations of heavy element J-couplings can now be performed for small- and medium-sized molecules using nonhybrid and hybrid density functional (DFT) methods.[4−9] However, much work remains to be done to determine reliable computational models that not only include relativistic effects in the NMR computations to a sufficient degree, but that also describe the sometimes very strong effects from the chemical environment of a metal complex or a metal−metal bonded moiety. These effects may include sizable "relativity−environment cross terms". Because of the aforementioned sensitivity of ^{199}Hg NMR parameters, their study is particularly useful to determine such computational models where there is a focus on relativistic effects.

In a previous computational study, it was shown that for a pristine $[Hg-Hg]^{2+}$ ion the one-bond coupling ^1J (^{199}Hg−^{199}Hg) may be as large as 0.9 MHz[10] (computations have demonstrated the lack of thermodynamic stability of the $[Hg-Hg]^{2+}$ ion in gas phase while the application of a continuum solvation model stabilizes the ion in solution[11]). However, to our knowledge the largest *measured* ^1J (^{199}Hg−^{199}Hg) coupling so far is 284.1(9) kHz for a complex of $[Hg-Hg]^{2+}$ with one 18-crown-6 and one 15-crown-5 ether (**1**) as reported by Malleier et al.[12] in 2001. Computations on this and a series of

---

† Current address: Academic Computer Centre CYFRONET Cracow, Poland.

(1) Granger, P. Groups 11 and 12: Copper to mercury. In *Transition Metal Nuclear Magnetic Resonance*; Pregosin, P. S., Ed.; Elsevier: Amsterdam, 1991.

(2) Wrackmeyer, B.; Contreras, R. *Annu. Rep. NMR Spec.* **1992**, *24*, 267−329.

(3) Bebout, D. C.; Berry, S. M. Probing mercury complex speciation with multinuclear NMR. In *Recent Developments in Mercury Science*; Structure Bonding, Vol. 120; Springer-Verlag: Berlin, 2006.

(4) Vaara, J.; Jokisaari, J.; Wasylishen, R. E.; Bryce, D. L. *Prog. Nucl. Magn. Res. Spectrosc.* **2002**, *41*, 233−304.

(5) Autschbach, J. The calculation of NMR parameters in transition metal complexes. In *Principles and Applications of Density Functional Theory in Inorganic Chemistry I*; Kaltsoyannis, N.; McGrady, J. E., Eds.; Structure Bonding, Vol. 112; Springer: Heidelberg, Germany, 2004.

(6) Autschbach, J.; Ziegler, T. *J. Chem. Phys.* **2000**, *113*, 936−947.

(7) Autschbach, J.; Ziegler, T. *J. Chem. Phys.* **2000**, *113*, 9410−9418.

(8) Filatov, M.; Cremer, D. *J. Chem. Phys.* **2004**, *120*, 11407−11422.

(9) Melo, J. I.; Ruiz de Azúa, M. C.; Peralta, J. E.; Scuseria, G. E. *J. Chem. Phys.* **2005**, *123*, No. 204112.

(10) Autschbach, J.; Igna, C. D.; Ziegler, T. *J. Am. Chem. Soc.* **2003**, *125*, 4937−4942.

(11) McKee, M. L.; Swart, M. *Inorg. Chem.* **2005**, *44*, 6975−6982.

(12) Malleier, R.; Kopacka, H.; Schuh, W.; Wurst, K.; Peringer, P. *Chem. Commun.* **2001**, 51−52.

10.1021/ja073166+ CCC: $37.00 © 2007 American Chemical Society

related model systems have shown that coordination by ligands, in particular in trans position to the metal−metal bond, and polarization of the metal−metal fragment lead to a strong reduction of J (^{199}Hg−^{199}Hg).[10] Good agreement between computations and experiment was achieved for complex **1**, with a computed spin-free relativistic one-bond coupling of 278.4 kHz.

The first ^{199}Hg−^{199}Hg coupling ever detected experimentally,[1] and for a long time the largest known nuclear spin−spin coupling constant, is the 139.7(3) kHz one-bond coupling in the [Hg−Hg−Hg]$^{2+}$ ion measured by Gillespie et al.[13] at −70 °C in liquid SO_2. DFT computations on $[Hg_3]^{2+}$ were performed in ref 10 with the VWN local density functional, yielding a gas-phase result for ^1J (^{199}Hg−^{199}Hg) of 241.0 kHz (spin−orbit relativistic calculation). The much smaller one-bond coupling compared to gas-phase [Hg−Hg]$^{2+}$ can be rationalized by the aforementioned influences of trans coordination (here by another Hg atom) and resulting polarization of the terminal Hg−central Hg metal−metal fragment. However, the computed result compares very poorly with the experimentally determined one-bond coupling constant of 139.7(3) kHz. Improved calculations were attempted in the earlier computational study, ref 10, by performing geometry optimizations of $[Hg_3]^{2+}$ with up to 10 solvent molecules or with two counterions (AsF_6^-). These calculations indicated that both the one-bond and two-bond J (^{199}Hg−^{199}Hg) of the $[Hg_3]^{2+}$ ion are very sensitive to the presence of solvent. The counterions had a similar effect. However, because of the large conformational space and the shallow solvent−solute interaction potentials the computations were deemed unreliable in providing an estimate for the coupling constants of the $[Hg_3]^{2+}$ system. In most of the computations the one-bond coupling was in fact much below the experimental value. Because of the formidable computational expense necessary to improve upon the models used in ref 10, it has so far remained an open question whether the J-couplings of the solvated $[Hg_3]^{2+}$ ion can be satisfactorily reproduced by any of the available DFT methods and what the requirements for a computational model would be.

The modeling of chemical−environment and vibrational effects on transition metal NMR chemical shifts has over in the past years indicated that computational protocols based on ab initio molecular dynamics (MD) with classically treated nuclei are very promising. For instance, Bühl and co-workers have computed a wide range of 3d and 4d metal chemical shifts with such techniques and in some cases obtained dramatic improvement over static computations based on optimized geometries.[15−20] We have recently started to explore the combination of relativistic NMR chemical shift DFT calculations with gradient-corrected functional in combination with MD-based averaging for ^{195}Pt chemical shifts.[21] To our knowledge, similar attempts to model solution NMR data for J-couplings involving sixth-row elements such as W, Pt, Hg, Tl, or Pb have not yet been made.

The purpose of this work is twofold. First, it will be demonstrated that good agreement with experiment can be achieved for ^1J (^{199}Hg−^{199}Hg) of the [Hg−Hg−Hg]$^{2+}$ ion solvated in SO_2 if MD simulations are employed. Averaged J-couplings were obtained here from a sequence of snapshots along a MD trajectory. It will be shown that the large difference between the calculated gas-phase coupling constant and the experimental value is almost entirely due to a preferred coordination of the terminal Hg atoms by the solvent at close range. The explicit consideration of dynamic solvent−solute interactions reduces the calculated coupling constant by roughly 90 kHz (a change corresponding to more than half of the experimental coupling constant) and brings the calculated average ^1J (^{199}Hg−^{199}Hg) within less than 10% deviation from experiment. Second, we will show that a continuum solvation model fails to describe this situation. The sensitivity of the Hg−Hg coupling, which is amplified by relativistic effects,[10] provides an excellent test case for the ability of first−principles computations to model the conditions under which experimental results for heavy atom NMR parameters are obtained. Therefore, the general purpose of this work is to show that the computational protocol as employed here is able to yield good agreement with experiment for J-couplings involving a heavy element in a situation where both relativistic effects and effects from the chemical environment are large.

The paper is organized as follows: In section 2 we provide details of our computations. The results are presented and discussed in section 3. The main focus will be on ^1J (^{199}Hg−^{199}Hg) because only this coupling constant has been measured experimentally. For completeness, we will also provide results for the two-bond coupling. A a few concluding remarks and a discussion of remaining sources of error in the computations can be found in section 4.

2. Computational Details

Ab initio Born−Oppenheimer molecular dynamics simulations (BOMD) of $[Hg_3]^{2+}$ and nine SO_2 solvent molecules were performed. Previous computational work on [Hg−Hg−Hg]$^{2+}$ has indicated that around 8−10 solvent molecules are necessary to provide a large enough solvation shell needed to reproduce the experimental one-bond coupling.[10] The BOMD driver program kindly provided by Prof. Tom Woo, University of Ottawa, Canada, contains an implementation of the velocity-version of the Verlet[22] algorithm and includes the Andersen thermostat.[23] Our local modifications of this code comprise interfaces with the Turbomole and ADF density functional packages[21] as well as the implementation of a barrier potential to prevent solvent molecules from "evaporating". The nuclei were treated as classical particles. Energies and forces used as input for the velocity Verlet MD were calculated with the Perdew−Burke−Ernzerhof (PBE) density functional[24−26] using the Turbomole package version 5.7.1.[27] The resolution of the identity (RI-) DFT implementation and accompanying TZVP (Hg) and SVP (S,O) basis sets[28] were employed. A 60-electron Stuttgart

---

(13) Gillespie, R. J.; Granger, P.; Morgan, K. R.; Schrobilgen, G. J. *Inorg. Chem.* **1984**, *23*, 887−891.
(14) Autschbach, J.; Igna, C. D.; Ziegler, T. *J. Am. Chem. Soc.* **2003**, *125*, 1028−1032.
(15) Bühl, M.; Parrinello, M. *Chem.−Eur. J.* **2001**, *7*, 4487−4494.
(16) Bühl, M.; Mauschick, F. T. *Phys. Chem. Chem. Phys.* **2002**, *4*, 5508−5514.
(17) Bühl, M.; Mauschick, F. T.; Terstegen, F.; Wrackmeyer, B. *Angew. Chem., Int. Ed.* **2002**, *41*, 2312−2315.
(18) Buehl, M.; Schurhammer, R.; Imhof, P. *J. Am. Chem. Soc.* **2004**, *126*, 3310−3320.
(19) Bühl, M. *J. Phys. Chem. A* **2002**, *106*, 10505−10509.
(20) Bühl, M.; Grigoleit, S.; Kabrede, H.; Mauschick, F. T. *Chem.−Eur. J.* **2006**, *12*, 477−488.
(21) Sterzel, M.; Autschbach, J. *Inorg. Chem.* **2006**, *45*, 3316−3324.
(22) Frenkel, D.; Smit, B. *Understanding Molecular Simulation;* Academic Press: San Diego, CA, 1996.
(23) Andersen, H. C. *J. Phys. Chem.* **1980**, *72*, 2384−2393.
(24) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865−3868.
(25) Zhang, Y.; Yang, W. *Phys. Rev. Lett.* **1998**, *80*, 890.
(26) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1998**, *80*, 891.
(27) Ahlrichs, R.; Bär, M.; Häser, M.; Horn, H.; Kölmel, C. *Chem. Phys. Lett.* **1989**, *162*, 165−169.

pseudopotential[29] was used for the mercury atoms. During the initial phase of the BOMD simulation, an ellipsoidal barrier with radii 7.5, 5.5, and 5.5 Å and a barrier force constant of 1.0 au was applied. The BOMD time step was chosen as 100 au or approximately 2.418 fs. The dynamics was performed as follows: step 0−2000, starting temperature 400 K, cooling until 200 K; step 2000−7000, temperature changes of ±10 K allowed, equilibration appeared to be reached around step 7000 (at that point total energy changes between successive time steps were $\leq 10^{-5}$ au); step 7000−15000, first tests of averaging coupling constants, temperature changes of ±2 K allowed by the thermostat but often exceeded. Monitoring of temperature fluctuations and *J*-coupling averages during the dynamics suggested that the barrier potential was set too tight. The ellipsoid radii were extended to 9.5, 7.5, 7.5 Å, the force constant was lowered to 0.1 au, and the system was re−equilibrated. Temperature fluctuations stayed within ±2 K. Step 15000−30000: production run. Graphics from the BOMD simulation were created with the VMD program.[30]

Between MD steps 15000 and 30000 every 50th configuration was selected for a calculation of *J* (^{199}Hg−^{199}Hg). For the spin−spin coupling calculations we have applied the Amsterdam Density Functional (ADF) program package[31] using the NMR code developed by Autschbach and Ziegler[6,7] which is based on the zeroth-order regular approximate (ZORA) relativistic Hamiltonian.[32] Both spin-free (scalar, ZSC) and spin-orbit ZORA (ZSO) calculations were performed with the revised PBE (revPBE) density functional. For S and O we have used a polarized valence triple-ζ (TZP) Slater-type basis set and for Hg a TZP basis augmented with an even-tempered set of 1s and 2p functions with exponents up to 6×10^4 as described in earlier computational studies of ^{199}Hg NMR parameters.[6,14,33−35] The high-exponent functions are very important to compute the correct magnitude of the hyperfine integrals for Hg (see, e.g., ref 36). The Slater-type basis sets applied in this work have previously been shown to yield good agreement with experimental data for Hg spin−spin coupling constants.[6,10,33,35] For ^{199}Hg chemical shifts the sensitivity of the computations to the basis set quality in the valence region appears to be somewhat more pronounced although the agreement with experiment that can be achieved by DFT computations of similar type as performed here (local nonhybrid functionals with Slater-type basis sets and relativistic effects treated by the ZORA Hamiltonian) is also quite reasonable overall.[34,37] For efficiency reasons, the response of the exchange-correlation (XC) potential was described on the basis of the Vosko−Wilk−Nusair (VWN) local density functional[38] after some test calculations indicated that gradient corrections to the exchange-correlation kernel had only a small influence on the calculated coupling constants. The ZORA analogs of the Fermi-contact (FC), spin-dipole (SD), paramagnetic (PSO), and diamagnetic spin-orbital (DSO) terms as well as the FC−PSO and SD−PSO spin-orbit cross terms[7,33] were included in the spin-orbit computations of the *J*-couplings. For the scalar relativistic ZORA computations, the SD term was neglected after test calculations showed that it is negligible for the coupling constants studied here. Reported *J*-couplings are based on a magneto−gyric ratio of 4.815×10^7 rad/(T s) for consistency with previous work on ^{199}Hg NMR parameters.[6,14,33−35] Using the currently accepted value of 4.846 $\times 10^7$ rad/(T s) would lead to a scaling of all coupling constants reported here by a factor of 1.013. An integration accuracy parameter of 5.0 and 6.0 (roughly indicating the number of significant figures for the electron density integration[39]) has been used for the valence and core regions, respectively, in the ground state and the *J*-coupling computations.

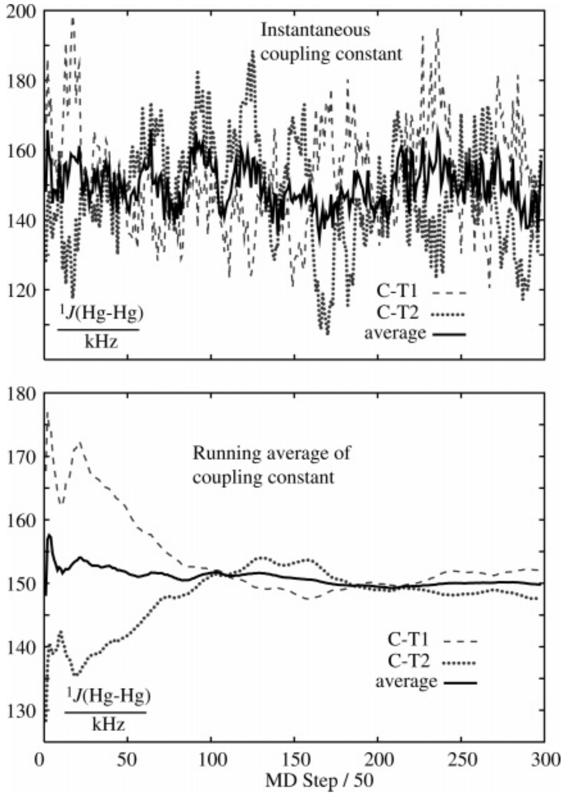

Figure 1. Instantaneous ^1J (^{199}Hg−^{199}Hg) (top) and running average (bottom) between central (C) and terminal (T1, T2) Hg atoms of [Hg−Hg−Hg]$^{2+}$ based on a configuration taken from the BOMD trajectory (PBE functional). Coupling constant was calculated at the ZSO/revPBE level of theory (see section 2 for details).

In addition to calculations with explicit solvent molecules, we have also applied the ADF implementation[40] of the conductor−like screening model (COSMO)[41] which is a continuum solvation model. A Hg radius of 1.86 Å was assigned to construct the solvent-accessible surface. We note that previous work has indicated that computed metal NMR parameters are not overly sensitive to the choice of the radii as long as they remain within reasonable limits.[42,43] Optimizations of [Hg$_3$]$^{2+}$ with and without the COSMO model employed the same integration parameters as the *J*-coupling computations and a 60-electron frozen core, gradient convergence 0.001 au/Å (rms and max), and no use of symmetry; otherwise default parameters were applied.

The following discussion is based on the computations which were carried out for this work with the PBE family of functionals.

3. Results and Discussion

The main results for ^1J (^{199}Hg−^{199}Hg) obtained from averaging 300 MD snapshots over a simulation time of 15000 time steps (roughly 36 ps) are shown in Figure 1. The coupling constants were calculated including relativistic effects from

---

(28) Eichkorn, K.; Treutler, O.; Öhm, H.; Häser, M.; Ahlrichs, R. *Chem. Phys. Lett.* **1995**, *242*, 652−660.
(29) Andrae, D.; Haeussermann, U.; Dolg, M.; Stoll, H.; Preuss, H. *Theor. Chem. Acc.* **1990**, *77*, 123−141.
(30) Humphrey, W.; Dalke, A.; Schulten, K. *J. Mol. Graphics* **1996**, *14*, 33−38.
(31) Baerends, E. J.; et al. *ADF2006.01, SCM, Theoretical Chemistry*; Vrije Universiteit: Amsterdam, The Netherlands; http://www.scm.com.
(32) van Lenthe, E.; Baerends, E. J.; Snijders, J. G. *J. Chem. Phys.* **1993**, *99*, 4597−4610.
(33) Autschbach, J.; Ziegler, T. *J. Am. Chem. Soc.* **2001**, *123*, 3341−3349.
(34) Jokisaari, J.; Järvinen, S.; Autschbach, J.; Ziegler, T. *J. Phys. Chem. A* **2002**, *106*, 9313−9318.
(35) Autschbach, J.; Kantola, A.; Jokisaari, J. *J. Phys. Chem. A* **2007**, *111*, 5343−5348.
(36) Autschbach, J. *Theor. Chem. Acc.* **2004**, *112*, 52−57.
(37) Wolff, S. K.; Ziegler, T.; van Lenthe, E.; Baerends, E. J. *J. Chem. Phys.* **1999**, *110*, 7689−7698.
(38) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200−1211.
(39) te Velde, G.; Baerends, E. J. *J. Comput. Phys.* **1992**, *99*, 84−98.
(40) Pye, C. C.; Ziegler, T. *Theor. Chem. Acc.* **1999**, *101*, 396−408.
(41) Klamt, A. *J. Phys. Chem.* **1996**, *100*, 3349−3353.
(42) Autschbach, J.; Le Guennic, B. *Chem.*−*Eur. J.* **2004**, *10*, 2581−2589.
(43) Autschbach, J.; Le Guennic, B. *J. Am. Chem. Soc.* **2003**, *125*, 13585−13593.

Table 1. Optimized Hg−Hg Internuclear Distance *R* and *J*-Couplings (for ^{199}Hg) of $[Hg-Hg-Hg]^{2+}$ from Static DFT Computations[a]

method	*R* (Å)	^1J (kHz)	^2J (kHz)
ZSC gas phase	2.776[b]	260.1	494.6
ZSO gas phase	2.776[b]	259.5	486.7
ZSC gas phase	2.670[c]	230.1	398.4
ZSC COSMO	2.670[c]	237.4−238.4[d]	348.5
ZSO COSMO	2.670[c]	236.3	344.5
exptl		139.7(3)[e]	N/A

[a] revPBE functional, TZP Slater−type basis set with high−exponent functions as described in section 2. Optimizations were performed at ZSC/revPBE level with TZP basis and 60−electron frozen core. N/A = not available. [b] Optimized in gas phase [c] Geometry was optimized using the COSMO model. Dielectric constant ϵ of 27.1 was used, from linear extrapolation of $\epsilon = 15.0$ at 273 K and $\epsilon = 17.6$ at 253−200 K. [d] ϵ varied between 15.0 and 100.0. [e] Experimental data from ref 13.

spin−orbit coupling. The final running average is just below 150 kHz and therefore within less than 8% deviation from experiment. Scalar ZORA calculations yielded very similar results, with the final average being roughly 2 kHz higher than the spin-orbit average.

For comparison with the BOMD average, Table 1 lists calculated gas-phase coupling constants and couplings obtained with the COSMO continuum solvent model. The gas-phase data differ somewhat from those reported in our previous paper[10] because a different density functional was applied in the geometry optimizations. The VWN functional was used in ref 10 whereas the PBE family of gradient functionals was used in this work. VWN leads to shorter Hg−Hg distances which results in smaller one-bond coupling constants. For reasons of consistency with the BOMD simulations we decided to base the comparison with gas phase and COSMO data on the same family of gradient functionals. The large disagreement with experiment for both the gas-phase and the COSMO computations of ^1J (^{199}Hg−^{199}Hg) is evident. Essentially all of the influence from the continuum solvent model is due to its effect on the Hg−Hg distance, which shortens by about 0.1 Å with a concomitant lowering of the one-bond coupling by 30 kHz (compare the gas-phase ZSC results based on gas-phase and COSMO geometry in Table 1). The electronic effect from the COSMO model on the *J*-coupling through changes of the ground-state orbitals *raises* the one-bond coupling, but only by about 8 kHz. This effect is rather insensitive to the dielectric constant used to describe the solvent and does not improve the results toward better agreement with experiment. In comparison, the 150 kHz for ^1J (^{199}Hg−^{199}Hg) obtained from the BOMD averaging, which appears to be stable after about 200 geometries have been averaged, agrees quite well with the experiment.

From the BOMD results shown in Figure 1 it is apparent that the solvent coordination of the two terminal Hg atoms is not completely equivalent, but the average ^1J (^{199}Hg−^{199}Hg) is well converged after averaging 300 configurations. As can be seen from the running averages of the individual one-bond couplings there is a very slow modulation of each coupling that appears to go along with a slow change in the bending of the $[Hg-Hg-Hg]^{2+}$ ion. A bending of the $[Hg-Hg-Hg]^{2+}$ ion is also visible in the animated graphics of the MD (see Supporting Information). The animation shows that the solvent−solute contact primarily involves the solvent's oxygen atoms. See Figure 2 for two snapshots of the BOMD in which typical solvent−solute contacts involving the terminal Hg atoms are visible. A plot of the radial distribution *d*(*r*) of oxygen atoms around the central and the terminal mercury atoms, Figure 3, reveals quite different oxygen distributions around the central and the terminal Hg atoms. In particular, strong peaks in *d*(*r*) are seen around 2.5 Å for the terminal Hg atoms. These peaks indicate close solvent−solute contacts, whereas the central Hg atom is less closely coordinated. This feature is, in a qualitative sense, also visible in the dynamics animation available in the Supporting Information. The radial distributions were normalized such that $\sum_i r_i^2 d(r_i) = 18$ for the 18 oxygen atoms in this system, with *r* being the distance from the Hg nucleus of interest. Up to a distance of 3.0 Å the partial summation yields 1.8 oxygen atoms for the central Hg but 3.1 oxygens for each terminal Hg atom (see integrated *d*(*r*) in Figure 3). Since there is more free space around the terminal Hg atoms, a higher average coordination of the terminal Hg atoms by solvent molecules at short to medium distances is expected. However, for the central Hg there are no oxygens found at the shortest distances (roughly between 2.4 and 2.6 Å) while for the terminal Hg atoms there are frequent solvent contacts at this close range. The static computations of ref 10 have already shown that local minimum structures with particularly close contacts between solvent and terminal Hg yielded the strongest reduction of the one-bond Hg−Hg coupling constants relative to the gas−phase value. At the same time, no minimum structures with a preferred coordination of the central Hg atom could be found. In the present work this situation is reflected by the lack of very close contacts between the solvent and the central Hg atom in the MD.

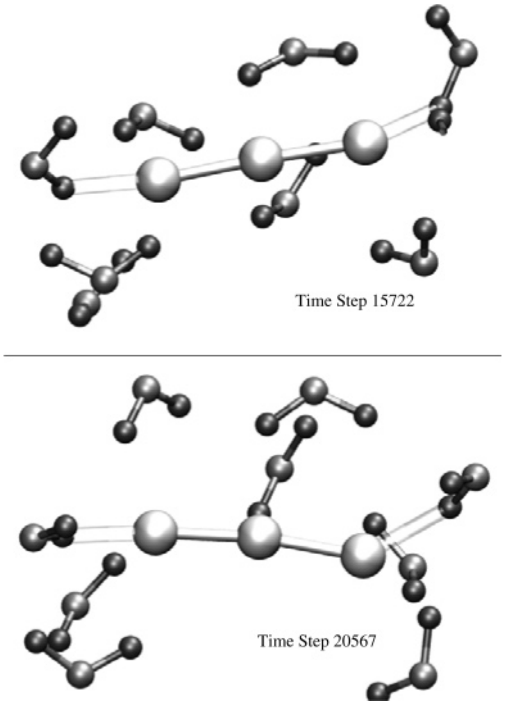

Figure 2. Two snapshots of the BOMD simulation on which the data shown in Figure 1 is based.

Ⓦ Close contacts between solvent and solute are indicated as translucent "weak-bond" sticks. An animated graphic in .avi format is available for viewing.

Consider a simple Hückel model for $[Hg-Hg-Hg]^{2+}$ with the three 6s atomic orbitals (AOs) on the central (C) and the

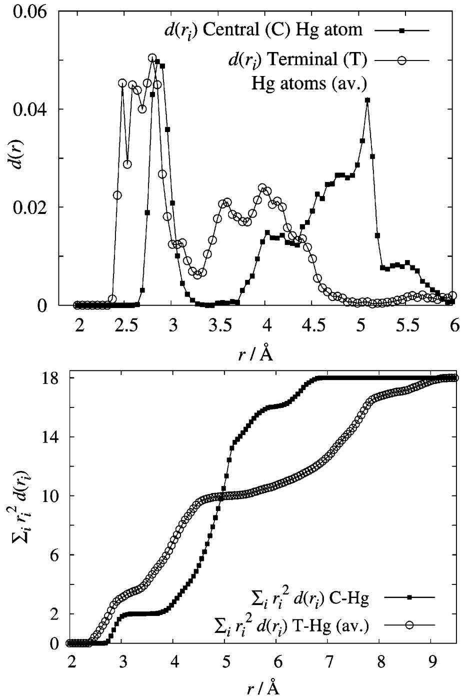

Figure 3. (Top) Radial distribution $d(r)$ of oxygen atoms belonging to the solvent around the central and the terminal (average is shown) Hg atoms of $[Hg-Hg-Hg]^{2+}$. (Bottom) Integrated $d(r)$ based on the BOMD simulation with nine SO_2 molecules for which J-coupling results are shown in Figure 1. The variable r is the distance from one of the Hg atoms.

two terminal Hg atoms (T1, T2). The two occupied Hückel orbitals are then

$$\varphi_1 = \frac{1}{2}(s_{T1} + \sqrt{2}s_C + s_{T2}) \tag{1a}$$

$$\varphi_2 = \frac{1}{\sqrt{2}}(s_{T1} - s_{T2}) \tag{1b}$$

It was already shown in ref 10 that one can predict a ratio of 1.5 for the two-bond over the one-bond Hg−Hg coupling constant from a Hückel model. The larger magnitude of ^2J is in qualitative agreement with the gas-phase and COSMO computations as well as with the BOMD averages (see below for a discussion of ^2J). From the two occupied orbitals, the Hückel AO populations are determined as $^3/_2$ for each terminal Hg atom and 1 for the central Hg atom. This leads to atomic charges of $+^1/_2$ for the terminal Hg atoms and +1 for the central Hg atom. In this simple model (no overlap considered), the relative higher concentration of electronic charge at the terminal Hg atoms appears to rationalize their preferred coordination by the solvent's oxygen atoms. However, the Hückel model has its limits, as seen by a comparison with the Mulliken gross charges of 0.75 and 0.50 for the terminal and the central Hg, respectively, or Hirshfeld charges of 0.72 and 0.56, as calculated at the ZSC level in the gas phase. Similar results are obtained in the COSMO computations, showing that the terminal Hg atoms are in fact slightly more positively charged than the central Hg. Therefore, the close contacts between oxygen and the terminal Hg atoms might simply have an electrostatic origin.

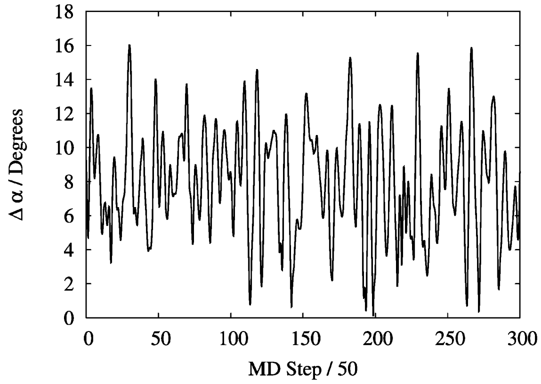

Figure 4. Deviation Δα of the Hg−Hg−Hg angle in $[Hg-Hg-Hg]^{2+}$ from 180° during the BOMD simulation with nine SO_2 molecules for which J-coupling results are shown in Figure 1.

The drastic lowering of ^1J ($^{199}Hg-^{199}Hg$) in the presence of SO_2 molecules is *not* related to a shortening of the average Hg−Hg distance beyond the difference between gas−phase and COSMO (Table 1). The running average of the Hg−Hg distance for the BOMD simulation is 2.70 Å (not shown in Figure 1), with the distances oscillating between 2.66 and 2.76 Å. This lies in between the gas-phase and COSMO optimized distances for which one-bond couplings in excess of 230 kHz are predicted in the absence of explicit solvation, see Table 1.

Figure 4 displays the deviation Δα of the Hg−Hg−Hg bond angle away from 180° during the production phase of the BOMD simulation. Deviations on the order of 8° are seen to be typical throughout the simulation. The solvent−solute contacts induce some bending of the $[Hg-Hg-Hg]^{2+}$ ion, which was also seen in the static computations reported earlier in ref 10. The apparent change of sign of the deviation near MD step 200 coincides with the second crossing of the central−T1 and central−T2 running averages in Figure 1. However, a visual comparison of plots of ^1J ($^{199}Hg-^{199}Hg$) versus MD step and Δα versus MD step did not reveal a clear correlation between the bending of the $[Hg-Hg-Hg]^{2+}$ ion and the variations on the one-bond couplings. According to additional ZSC COSMO computations that we performed, the bending itself is also *not* the source for the lowering of the one-bond coupling constant. Calculations with Hg−Hg−Hg angles of 5, 8, and 15° yielded ^1J ($^{199}Hg-^{199}Hg$) values of 238.3, 238.4, and 239.0 kHz, respectively.

It is therefore reasonable to conclude that close-contact electronic interactions between solvent and solute beyond the electrostatic effects that are included in the continuum model are responsible for most of the drastic lowering of ^1J ($^{199}Hg-^{199}Hg$) in solution. Computations that attempt to reproduce experimental NMR data for this and similar systems therefore need to consider the solvent on a quantum-mechanical level and include at least one explicit solvation shell. A problem with straightforwardly combining the explicit solvation with the COSMO continuum solvent model as it is implemented is the difference in the average distances between the solvent and the Hg atoms during the MD. One would need to ascertain that no artificial continuum model surface is created between the $[Hg_3]^{2+}$ ion and any of the explicit solvent molecules.

The two-bond coupling is not detectable in $[Hg-Hg-Hg]^{2+}$ due to symmetry. We decided to restrict the MD averaging to

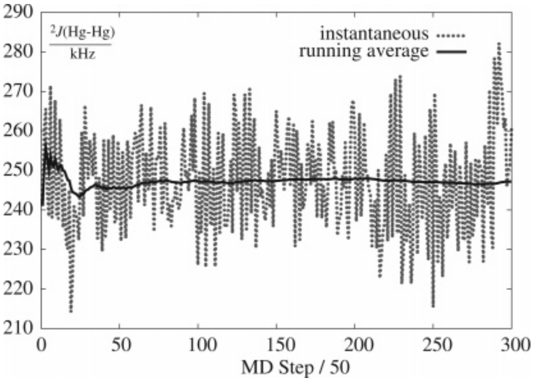

Figure 5. Two-bond coupling ^2J (^{199}Hg−^{199}Hg) in [Hg−Hg−Hg]$^{2+}$ from the BOMD simulation on which the data shown in Figure 1 is based. Instantaneous coupling and running average calculated at ZSC/revPBE level.

the less expensive spin-free relativistic level. Figure 5 shows the averaged two-bond coupling obtained from the BOMD simulation. The final running average is 247 kHz. Results from static computations (gas phase and COSMO) are listed in Table 1. It is clear that ^2J (^{199}Hg−^{199}Hg) is also severely affected by the same solvent coordination effects that cause the one-bond coupling to drop by about 90 kHz. The reduction of the two-bond coupling relative to the computed gas-phase value amounts to about half of the gas-phase coupling's magnitude. The COSMO computations yield somewhat more improvement over the gas-phase computations than it was found for the one-bond coupling. The COSMO coupling constant of 349 kHz (ZSC) is, however, still more than 100 kHz larger than the BOMD result. As in the case of the one-bond coupling, the data in Table 1 show that most of the COSMO effect is due to its influence on the optimized geometry, although for the two-bond coupling its electronic effect is also considerable and reduces the coupling further.

4. Concluding Remarks

Overall, the agreement with experiment obtained from the BOMD−based averaging of the one-bond spin−spin coupling constants in [Hg−Hg−Hg]$^{2+}$ is very satisfactory. The improvement over static computations including solvent molecules that were performed previously[10] is considerable: all of the computed one- and two-bond couplings reported in ref 10 based on optimized structures ([Hg$_3$]$^{2+}$ with varying numbers of solvent molecules) were below (in many cases significantly below) the BOMD averages obtained here. This highlights the importance of averaging the NMR parameters with configurations both close to and far away from the potential-energy surface minima contributing to the final average. Some possible reasons for the remaining differences with experiment are (i) the effects from contacts between [Hg$_3$]$^{2+}$ and a counterion may be larger than the solvent−contact effect. However, a much larger solvation shell would be needed to study the competition between the two influences which is not feasible at this time. Our preliminary data[10] have indicated that similar effects are obtained from surrounding the [Hg$_3$]$^{2+}$ ion with SO$_2$ solvent molecules or counterions. (ii) A larger solvation shell might be needed to further reduce the one-bond coupling. (iii) Previous work has indicated that the Hg−Hg distances are somewhat overestimated by the GGA functional applied here.[10] A shortening (on average) might lead to a further reduction of the *J*-coupling constants. However, we have seen in section 3 that the main solvent effect is not due to geometry changes upon solvation. (iv) A point-nucleus model was adopted in the computations. Using a finite-nucleus model is expected to reduce the calculated coupling constants somewhat. However, the basis set truncation near the nucleus partially compensates for the missing finite-nucleus model.[6] (v) As always, approximations in the density functional and the exchange-correlation kernel had to be made which have an influence on the accuracy of the computed results. Work on heavy metal NMR parameters performed over the past years has indicated that comparatively simple functionals perform quite well for the high electron-density regime in heavy atomic systems and also appear to perform well for describing the effect of close-contact solvent−solute effects on the NMR parameters of the solute. (vi) More specific to the molecular dynamics, gradient-corrected (GGA) functionals such as the PBE functional employed in this work do not properly describe dispersion effects. Their asymptotic behavior may also lead to inaccuracies in the solvent−solute potentials affecting the *J*-coupling average. In computational studies of water and aqueous solutions it has in been shown that dynamics performed with GGA functionals such as PBE, BP, or BLYP can yield reasonable properties of liquids and solutions[44−48] and be instrumental in NMR chemical shift averaging,[20] although improved results are likely to be obtained with MD based on hybrid functionals[49,50] or from GGAs optimized for condensed-phase simulations.[50] Improvements from more accurate intermolecular potentials might be expected for the simulation of [Hg$_3$]$^{2+}$ in liquid SO$_2$ provided that there are no adverse effects on the intrinsic *J*-couplings. (vii) Intermolecular vibrational motions as well as other nuclear motions were treated in the MD as classical motions, although the forces were obtained quantum mechanically. For the free [Hg$_3$]$^{2+}$ ion (gas phase) using the computational technique described in refs 51 and 52, we have estimated the zero-point vibrational corrections on the Hg−Hg coupling constants to be within 1% of the equilibrium values and therefore negligible at the level of accuracy of our computation. Regarding the solvent−solute interactions in the MD, on the basis of the mass of the nuclei of the solvent we also expect rather small quantum effects of the solvent dynamics that could potentially influence the Hg *J*-coupling constants. See ref 20 for a related discussion of NMR metal chemical shift averaging in aqueous solution and comparisons with zero-point averaging. In summary, without simultaneously improving over most, if not all of the mentioned approximations it is unlikely that better agreement with experiment would be obtained for the right reasons.

Acknowledgment. We acknowledge support from the Center of Computational Research at SUNY Buffalo and financial

---

(44) Geissler, P. L.; Dellago, C.; Chandler, D.; Hutter, J.; Parrinello, M. *Science* **2001**, *291*, 2121−2124.
(45) Schwegler, E.; Grossman, J. C.; Gygi, F.; Galli, G. *J. Chem. Phys.* **2004**, *121*, 5400−5409.
(46) Lee, H. S.; Tuckerman, M. E. *J. Chem. Phys.* **2006**, *125*, No. 154507.
(47) Lee, H. S.; Tuckerman, M. E. *J. Chem. Phys.* **2007**, *126*, No. 164501.
(48) Gourlaouen, C.; Gerard, H.; Parisel, O. *Chem.−Eur. J.* **2006**, *12*, 5024−5032.
(49) Todorova, T.; Seitsonen, A. P.; Hutter, J.; Kuo, I. F. W.; Mundy, C. J. *J. Phys. Chem. B* **2006**, *110*, 3685−3691.
(50) Dahlke, E. E.; Truhlar, D. G. *J. Phys. Chem. B* **2005**, 109, 15677−15683.
(51) Mort, B. C.; Autschbach, J. *J. Phys. Chem. A* **2005**, *109*, 8617−8623.
(52) Mort, B. C.; Autschbach, J. *J. Am. Chem. Soc.* **2006**, *128*, 10060−10072.

support from the CAREER program of the National Science Foundation (Grant No. CHE−0447321). We thank Prof. Tom Woo (Ottawa) for providing us with his BOMD program and for helpful comments at an early stage of this project. We thank Brendan Mort for calculating the zero-point vibrational corrections of the *J*-couplings of $[Hg_3]^{2+}$. A preliminary set of computations for this work was performed at the Molecular Sciences Computing Facility (MSCF) of the Environmental Molecular Science Laboratory as part of the Grand Challenge project “Reliable Relativistic Quantum Chemistry Calculations for Molecules with Heavy Elements”.

Supporting Information Available: Animated graphics (AVI format, Windows Media compatible) showing part of the molecular dynamics of the $[Hg_3]^{2+}$ ion with nine SO_2 molecules in an ellipsoidal box, and complete ref 31. This material is available free of charge via the Internet at http://pubs.acs.org.

JA073166+