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NMR Measurements and Density Functional Calculations of the ^{199}Hg−^{13}C Spin−Spin Coupling Tensor in Methylmercury Halides

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The isotropic average, $J_{\mathrm{HgC}}^{\mathrm{iso}}$, and the anisotropy, ΔJ_{HgC}, of the ^{199}Hg−^{13}C spin−spin coupling tensor in methylmercury halides, CH_3HgX (X = Cl, Br, I), were determined for the first time by utilizing the NMR spectra of these molecules dissolved in liquid crystals. Furthermore, density functional calculations were performed using the zeroth-order regular approximation, including also dimethylmercury. The temperature-dependence of the $J_{\mathrm{HgC}}^{\mathrm{iso}}$ couplings in the isotropic phase was studied in each case in order to extrapolate their values into the liquid crystal state. Good agreement is found between the experimental and the calculated ΔJ_{HgC} values as long as solvent effects are considered in the computations. Most of the magnitude of ΔJ can be attributed to the spin mechanism of J-coupling, with additional sizable spin−orbital cross terms due to electronic spin−orbit coupling.

Introduction

Nuclear magnetic shielding and nuclear spin−spin coupling are tensor quantities. However, NMR experiments carried out in conventional isotropic liquid solutions yield exclusively scalar quantities, viz., the isotropic nuclear magnetic shielding constants (σ_K) and indirect spin−spin coupling constants (J_{KL}) for nuclei K, L, ... Consequently, theoretical calculations often concentrate on these quantities. However, much more information about the electronic structure of a molecule and about the range of applicability of computational methods can be gained if the complete tensor or at least its diagonal elements are available. This applies in particular to heavy nucleus systems where spin−orbit coupling and scalar relativistic effects can have a great influence on both the isotropic quantities as well as on the tensor properties.

NMR spectroscopy of solute molecules in liquid crystals (LCNMR, see, e.g., ref 1), that is, in anisotropic liquids, is a very applicable method to investigate spin−spin coupling tensors.[2−4] Namely, the experimentally detected anisotropic coupling, $D_{\mathrm{KL}}^{\mathrm{exp}}$, between the interacting nuclei K and L includes a contribution, $(^1/_2)J_{\mathrm{KL}}^{\mathrm{aniso}}$, from the respective indirect (electron-mediated) nuclear spin−spin coupling tensor

$$D_{\mathrm{KL}}^{\mathrm{exp}} = D_{\mathrm{KL}}^{\mathrm{dir}} + \frac{1}{2}J_{\mathrm{KL}}^{\mathrm{aniso}} \qquad (1)$$

Here, $D_{\mathrm{KL}}^{\mathrm{dir}}$ is the direct dipole−dipole coupling,

$$D_{\mathrm{KL}}^{\mathrm{dir}} = -\frac{\mu_0 \hbar \gamma_K \gamma_L}{8\pi^2}\left\langle \frac{s_{\mathrm{KL}}}{R_{\mathrm{KL}}^3} \right\rangle \qquad (2)$$

where $\langle\cdots\rangle$ indicates averaging over molecular reorientational and vibrational motions. The quantity s_{KL} in eq 2 describes the momentaneous orientational order of the internuclear vector $\mathbf{R}_{\mathrm{KL}}$ with respect to the external magnetic field $\mathbf{B}_0$. In general, it is customary to express the orientation with respect to the nematic director, **n**, but here s_{KL} is written directly with respect to $\mathbf{B}_0$ as the LCs used in this study orient along the magnetic field ($\mathbf{n} \| \mathbf{B}_0$), thus simplifying the equations. In a molecule fixed coordinate system (xyz), s_{KL} can be represented as

$$s_{\mathrm{KL}} = \sum_{\alpha\beta}^{xyz} s_{\alpha\beta}\cos(\theta_{\mathrm{KL},\alpha})\cos(\theta_{\mathrm{KL},\beta}) \qquad (3)$$

where $\theta_{\mathrm{KL},\alpha}$ is the angle between the $\mathbf{R}_{\mathrm{KL}}$ and the α axis, and

$$s_{\alpha\beta} = \frac{1}{2}(3\cos\theta_{\mathrm{B},\alpha}\cos\theta_{\mathrm{B},\beta} - \delta_{\alpha\beta}) \qquad (4)$$

When neglecting the correlation of the reorientational and vibrational motions, which causes the so-called deformational effects that will be discussed later, the average $\langle s_{\mathrm{KL}} R_{\mathrm{KL}}^{-3}\rangle$ can be replaced by $\langle s_{\mathrm{KL}}\rangle\ \langle R_{\mathrm{KL}}^{-3}\rangle$, where the first term leads to the definition of a traceless and symmetric Saupe orientational order tensor,[5]

$$\langle s_{\alpha\beta}\rangle = S_{\alpha\beta} = \frac{1}{2}\langle 3\cos\theta_{\mathrm{B},\alpha}\cos\theta_{\mathrm{B},\beta} - \delta_{\alpha\beta}\rangle \qquad (5)$$

The number of independent orientational order tensor elements depends upon the symmetry of the molecule under investigation.[4] The symmetry of the present methylmercury halides is C_{3v}, which means that only one tensor element is sufficient for the complete description of the orientation. When choosing the molecule-fixed coordinate system so that the z-axis coincides with the 3-fold symmetry axis, that is, with the C−Hg−X axis,

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the tensor element is S_{zz}. Then the anisotropic contribution from the ^{199}Hg−^{13}C indirect spin−spin coupling tensor to the respective D^{exp} coupling in eq 1 simplifies to

$$J_{\mathrm{HgC}}^{\mathrm{aniso}} = \frac{2}{3}\Delta J_{\mathrm{HgC}} S_{zz} \tag{6}$$

where the anisotropy of the J-coupling tensor is defined as $\Delta J_{\mathrm{HgC}} = J_{\mathrm{HgC},zz} - (^1/_2)(J_{\mathrm{HgC}xx} + J_{\mathrm{HgC},yy})$. Consequently, eqs 1 and 6 lead to

$$\Delta J_{\mathrm{HgC}} = 3\frac{D_{\mathrm{HgC}}^{\mathrm{exp}} - D_{\mathrm{HgC}}^{\mathrm{dir}}}{S_{zz}} \tag{7}$$

As stated above, the experimental dipole−dipole coupling is an average over vibrational and reorientational motions. For small amplitude motions, the various contributions can be separated, and the coupling can be represented in the form

$$D_{\mathrm{KL}}^{\mathrm{dir}} = D_{\mathrm{KL}}^{\mathrm{eq}} + D_{\mathrm{KL}}^{\mathrm{ah}} + D_{\mathrm{KL}}^{\mathrm{h}} + D_{\mathrm{KL}}^{\mathrm{d}} \tag{8}$$

where D^{eq} is the dipole−dipole coupling corresponding to the equilibrium structure of the molecule, D^{ah} arises from the anharmonicity of the vibrational potential, D^{h} is the contribution from the harmonic vibrations, and D^{d} is the deformation contribution due to the correlation of the vibrational and reorientation motions.

^{1}H and ^{13}C NMR spectra of the methylmercury halides dissolved in a liquid crystal were studied already in the late 1970s,[6] but in those days, the sensitivity of the available spectrometer was not sufficient (and, furthermore, the solubility of the compounds in liquid crystals is very low) for the detection of the ^{13}C satellites or the ^{199}Hg satellites in the ^{199}Hg or ^{13}C spectra, respectively. Recently, the ^{199}Hg shielding anisotropy of these molecules was investigated by LCNMR and computations.[7] The experimental results, taking into account harmonic vibrational corrections in the D^{exp} couplings, yield a decreasing shielding tensor anisotropy in the order $\Delta\sigma_{\mathrm{Hg}}(\mathrm{Me_2Hg}) > \Delta\sigma_{\mathrm{Hg}}(\mathrm{MeHgCl}) > \Delta\sigma_{\mathrm{Hg}}(\mathrm{MeHgBr}) > \Delta\sigma_{\mathrm{Hg}}(\mathrm{MeHgI})$, the value in the first case being as high as about 7300 ppm.[8,9] This trend in the behavior could be reproduced by calculations only when electronic spin−orbit coupling is taken into account.[7]

The ^{199}Hg−^{13}C spin−spin coupling tensor, i.e., its isotropic average and anisotropy, in dimethylmercury was studied earlier in four liquid-crystalline environments.[9] A slight solvent dependence in the quantity was found, but there are strong arguments for that the “best” value of ΔJ_{HgC} is 855 Hz, yielding a relative anisotropy $\Delta J_{\mathrm{HgC}}/J_{\mathrm{HgC}}$ of 1.23. Relativistic extended Hückel (REX) and REX−NMR calculations lead to a value of 1.34 for the latter quantity,[9] demonstrating that the anisotropy of the coupling tensor is large. Another study dealing with the ^{199}Hg−^{13}C spin−spin coupling tensor was carried out for methylmercury nitrate, $\mathrm{MeHgNO_3}$, in a nematic and in a lyotropic LC.[10] It was observed that the coupling constant J_{HgC} increased from 1697 ± 10 Hz to 1794 ± 1 Hz, i.e., by ca. 5.7%, when moving from the isotropic phase of the LC to aqueous solution (the lyotropic LC used contained about 52 wt % $\mathrm{D_2O}$). On the contrary, the anisotropy of the coupling tensor decreased from 582 ± 100 to 325 ± 50 Hz from the nematic to the lyotropic LC. These changes were explained by rehybridization of mercury.

The computation of spin−spin coupling tensors involving nuclei as heavy as Hg requires a relativistic theoretical framework. To date, most direct comparisons of theoretical spin−spin coupling data with experiment for J-couplings involving a heavy nucleus have been based on DFT calculations using the variationally stable zeroth-order regular approximate (ZORA) relativistic Hamiltonian as implemented by Autschbach and Ziegler.[14] See also a review concerned with spin−spin coupling by Vaara et al.[4] More recently, implementations for J-coupling based on higher-order regular approximations[15] and the Douglas−Kroll−Hess Hamiltonian[16] have been reported. For details on NMR calculations based on perturbation theory see, e.g., ref 17. Regarding the approximate relativistic treatment at the ZORA level, it has been shown that the ZORA hyperfine integrals for neutral heavy atoms are very similar to the ones obtained from a fully relativistic calculation that would be equivalent otherwise in terms of the basis functions and density functional that are applied.[18] This means that the major approximation in such calculations is likely not the treatment of relativity but the computational model otherwise, such as the level of exchange-correlation, basis sets, and external effects, most notably from solvents. Regarding early theoretical work on relativistic effects of Hg−ligand coupling constants and coupling anisotropies, see Pyykkö, ref 19. This work indicated that the relative anisotropy of the Hg−C coupling tensor increases due to relativistic effects, mainly due to a sizable contribution to ΔJ from spin−orbit coupling. The number of ab initio computational studies on Hg−ligand coupling tensors performed so far is rather limited. For isotropic spin−spin coupling constants involving one or two Hg atoms, Autschbach et al. have shown that scalar relativistic DFT calculations with standard nonhybrid functionals are able to achieve good agreement with experiment for a variety of systems.[14,20−22] For systems with open coordination sites such as X−Hg−Y, it was demonstrated that an explicit treatment of Hg solvent coordination is essential in order to achieve agreement with experimental data obtained from solution.[20,21] In general, the stronger coordinating the solvent, the larger a sizable (and generally positive) shift of the isotropic Fermi-contact term was obtained for metal−ligand coupling constants. Whether metal−ligand spin−spin coupling *tensors* are equally well reproduced by DFT calculations, and whether solvent effects on the coupling anisotropies are sizable or not, remain open questions. Thus, along with the experimental efforts reported in this paper, we have also studied Hg−ligand spin−spin coupling tensors computationally.

In the present paper, we extent the experimental investigation of the ^{199}Hg−^{13}C spin−spin coupling tensors to methylmercury halides, MeHgX (X = Cl, Br, I). LCNMR experimental results as well as ZORA DFT calculation results are reported. Acceptable agreement is found between the experimental and the calculated results for the anisotropies of the spin−spin coupling tensors.

Experimental and Theoretical

NMR Experiments. Methylmercury halides were purchased from Aldrich and the Phase 4 liquid crystal (eutectic mixture of *p*-methoxy-*p*′-*n*-butylazoxybenzenes) from Merck, and they were used without further purification. Phase 4 liquid crystal was chosen because it appeared to be a good solvent in the study of Hg−C coupling anisotropy in dimethylmercury. The samples were made into medium-wall 10 mm (o.d.) NMR tubes. The concentration of the solute varied from 2.7 to 4.4 mol %. All the samples were carefully degassed and finally sealed with a flame.

All of the spectra were recorded on a Bruker Avance DSX300WB spectrometer. Isotropic ^{199}Hg, ^{13}C, and {^{1}H}−^{13}C spectra were measured at 3−4 different temperatures ranging from 368 to 390 K. Temperature was calibrated with a calibration sample of 80% ethylene glycol in DMSO. Anisotropic ^{1}H and ^{13}C spectra were measured at 300 K (for CH_3HgI) or 310 K (for CH_3HgCl and CH_3HgBr). The typical number of scans accumulated was 20k for isotropic ^{13}C and ^{199}Hg spectra, 80k for anisotropic ^{13}C spectra, and 64 for anisotropic ^{1}H spectra. Each NMR spectrum was analyzed using the total line shape fitting mode of the PERCH software[12,13] to obtain the experimental splittings.

ZORA DFT Calculations. ZORA DFT calculations of Hg−C coupling tensors were performed with the program code implemented in the Amsterdam Density Functional (ADF) package[23] as described in refs 14 and 20. All relevant operators for the perturbation of the system by nuclear spins have been included. These are the ZORA analogs of the Fermi-contact (FC), spin−dipole (SD), paramagnetic spin−orbital (PSO), and diamagnetic spin−orbital (DSO) coupling mechanisms, the FC−SD cross term, which is very important for obtaining correct coupling anisotropies, as well as the FC−PSO and SD−PSO cross terms, which are mediated by spin−orbit coupling. The Vosko−Wilk−Nusair (VWN)[24] local density functional was applied to determine the unperturbed molecular orbitals as well as the first-order perturbed exchange−correlation potential. Note that in previous work on Hg−C couplings, the Slater Xα potential was applied to calculate the perturbed exchange potential. Therefore, there are small deviations between the present and previously reported isotropic coupling constants.[14,20] Computational results reported in refs 14 and 20 did not demonstrate a clear improvement for heavy metal−ligand coupling constants when using a density-gradient corrected (GGA) functional for the determination of the unperturbed orbitals. The investigations reported in ref 14 and followup work[22] showed that gradient functionals improve the coupling tensors significantly for systems where the PSO term dominates, while local-density and GGA functionals tend to yield similar results for heavy atom−ligand couplings in cases where the FC−SD spin mechanism is dominant, which is the case for the Hg systems studied here. We have therefore restricted this work to the use of the VWN density functional. In related work on Hg spin−spin coupling,[21] we have also obtained very satisfactory agreement with experiment for isotropic coupling constants with the VWN functional, with rather insignificant changes when gradient functionals were employed instead.

The ZORA spin−spin coupling calculations were carried out with the TZP basis of the ADF basis set library.[23] TZP is a triple-ζ valence/double-ζ core all-electron Slater basis augmented with one set of polarization functions (6p for Hg, 2p for H, nd for C, Cl, Br, I). For the J-coupling calculations, the Hg basis set was augmented with tight s- and p-functions as described in ref 14a, which is essential to obtain reasonable relativistic results for the Hg−ligand FC mechanism. It was previously shown that solvent effects are important to model Hg−ligand couplings.[20] Optimized geometries for the Me−Hg−Cl complexes, including three DMSO molecules, were taken from ref 20 and used as a starting point for optimizing the $X =$ Br, I and the $HgMe_2$ systems with 3 DMSO molecules at the ZORA/VWN/TZP level of theory. Unfortunately, due to the size of the liquid crystal molecules, it is not easily possible to simulate the solvation of the Hg complexes in the LCNMR experiments explicitly, but by a comparison for results obtained with and without a standard solvent, it is possible to determine if the coupling anisotropy is affected at all by solvent effects. We will show later that this is indeed the case, but to a lesser extent than for the isotropic coupling constants. Previous work on solvent effects has indicated that the solvent effects are rather unspecific, despite their magnitude.[20] Therefore, we assume that the coupling anisotropies calculated for the complexes in DMSO will be similar to those in the LC environment.

TABLE 1: Spin−Spin Coupling Constants $^2J_{HgH}$ and $^1J_{HgC}$ of the Methylmercury Halides at Variable Temperatures in the Isotropic Phase of the Phase 4 LC

compound	T (K)	$^2J_{HgH}$	$^1J_{HgC}$
MeHgCl	390	−201.6	1429.6
	382	−201.9	1432.2
	375	−202.0	1432.3
	368	−203.2	1434.8
MeHgBr	390	−195.2	1389.9
	382	−197.2	1391.1
	375	−198.3	1395.1
	368	−197.8	1397.8
MeHgI	382	−187.3	1318.2
	375	−187.6	1319.5
	368	−187.6	1322.3

TABLE 2: Extrapolated Spin−Spin Coupling Constants and Experimental Couplings as Determined from the NMR Spectra of the Methylmercury Compounds in the Phase 4 LC at 300 K (MeHgI) and 310 K (MeHgCl and MeHgBr)[a]

MeHgX, $X =$	Cl	Br	I	Me[b]
$^1J_{CH}$	139.1	139.2	142.5	
$(2D_{CH}^{exp} + J_{CH})$	3690.26	3589.36	3894.21	
$^2J_{HgH}$	−206.5	−205.7	−188.9	−102.2
$(2D_{HgH}^{exp} + J_{HgH})$	−638.6	−614.1	−637.9	
$^1J_{HgC}$	1447.3	1419.3	1341.9	693.8
$(2D_{HgC}^{exp} + J_{HgC})$	1341.2	1299.7	1214.6	

[a] See experimental section for details. [b] From ref 9.

Results and Discussion

The experimental isotropic J_{CH} couplings were obtained from ^{13}C spectra, J_{HgC} couplings from the ^{199}Hg satellites in {^{1}H}−^{13}C spectra, and J_{HgH} couplings from ^{199}Hg spectra. Because the isotropic spin−spin couplings, especially J_{HgC}, needed for the analysis of the anisotropic spectra appear to be stongly dependent on the temperature, their values at 300 K (for CH_3HgI) and 310 K (for CH_3HgCl and CH_3HgBr) were derived by linear extrapolation from the spectra determined at 3−4 different temperatures in the isotropic phase. In this way, the experimental anisotropic couplings, D_{HgH}^{exp}, D_{HC}^{exp}, and D_{HgC}^{exp}, can be obtained with better accuracy than if the J_{KL} values from the isotropic phase were used. Table 1 lists the values of the coupling constants $^2J_{HgH}$ and $^1J_{HgC}$ of the three studied systems at variable temperatures. The standard errors obtained from the spectral analysis varied between 0.1 and 0.9 Hz (0.02−0.5%) for these couplings.

The anisotropic D_{CH}^{exp} and D_{HgC}^{exp} couplings were obtained from the ^{13}C spectra, and the D_{HgH}^{exp} couplings from the ^{1}H spectra. The isotropic spin−spin couplings extrapolated to anisotropic temperatures, J_{KL}, and measured total experimental couplings, $2D_{KL}^{exp} + J_{KL}$, are listed in Table 2. The relative errors for the measured splittings were less than 0.2% and for the extrapolated spin−spin couplings under 1%, 3%, and 19% for J_{CH}, J_{HgC}, and J_{HgH}, respectively.

All of the direct dipolar couplings, D_{KL}^{dir}, were corrected for harmonic vibrations. The correction coefficients were adopted from ref 9. The anharmonic contributions can be included in the analysis either by calculating the correction coefficients from an anharmonic force field or by using an effective r_α geometry instead of the equilibrium geometry in the analysis. The latter approach was utilized in this study. The r_{CH}^{α} bond length was adopted from previously determined geometry for $(CH_3)_2Hg$.[9]

TABLE 3: Geometry Parameters and Harmonic Correction Coefficients Used in the Analysis of the Experimental Data[a]

compound	r_{HgC}	θ_{HCH}	p_{HgC}	p_{HgH}	p_{CH}
MeHgCl	2.061	110.61	0.036	0.039	0.108
MeHgBr	2.074	110.67	0.052	0.053	0.126
MeHgI	2.087	110.83	0.056	0.057	0.130

[a] All bond lengths in Ångstroms. $r_{CH} = 1.097$ Å for all compounds, from ref 9. $p_{KL} = D^{h}_{KL}/D^{eq}_{KL}$. The geometry parameters and the harmonic correction coefficients were adopted from Ref 7.

TABLE 4: Experimental D^{exp}_{HgC} Couplings, Direct Dipolar Couplings Corrected for Harmonic Vibrations D^{dir}_{HgC}, and Anisotropic Part of Spin−Spin Coupling J^{aniso}_{HgC} of the Methylmercury Compounds in the Phase 4 LC at 300 K (MeHgI) and 310 K (MeHgCl and MeHgBr)[a]

compound	D^{exp}_{HgC}	D^{dir}_{HgC}	J^{aniso}_{HgC}
MeHgCl	−53.0	−147.4	188.7
MeHgBr	−59.8	−140.2	160.8
MeHgI	−63.7	−148.6	170.0

[a] See Experimental Section for details.

Other necessary geometry parameters (r^{α}_{HgC} and θ^{α}_{HCH}) for the r_{α} geometries specific to each molecule were taken from ref 7. The geometry parameters together with the harmonic correction coefficients utilized in the experimental analysis are listed in Table 3.

The orientation parameters, S_{zz}, were calculated from the D^{dir}_{CH} couplings corrected for harmonic vibrations. Even though the Hg−H couplings were also measured, C−H couplings were chosen as they were more accurately determined (i.e., smaller error arising from the extrapolation) and there is also no prior knowledge of the anisotropic contribution to the spin−spin coupling tensor for the Hg−H couplings. On the other hand, the anisotropy of the spin−spin coupling J^{aniso}_{CH} can be ignored in the analysis, as it has been shown to be insignificant ($J^{aniso}_{CH}/D^{exp}_{CH} \simeq 10^{-3}$).[2] Generally the rotation−vibration correlation (deformation) can affect the observed dipolar couplings up to several percent. However, because of lack of information, the deformation effects were excluded from the analysis, but for strongly oriented molecules of C_{3v} symmetry, as is the case in this study, they are likely to give less than 1% contribution to the S_{zz} determined from D_{CH} coupling. The importance of the anisotropies of the ^{199}Hg−^{1}H spin−spin couplings was tested by replicating the analysis, but using the D^{exp}_{HgH} couplings to calculate the orientation parameters. The final results for the anisotropies of the ^{199}Hg−^{13}C spin−spin couplings varied less than 2% from the results presented here, indicating a comparatively small relative anisotropy $J^{aniso}_{HgH}/D^{exp}_{HgH}$. The accuracy of the experimental data, especially for the extrapolated isotropic spin−spin coupling constants, was not adequate to enable determination of the values for ΔJ_{HgH} with reasonable accuracy.

The experimental ^{199}Hg−^{13}C couplings, D^{exp}_{HgC}, the respective calculated direct dipolar couplings with harmonic vibrational corrections, D^{dir}_{HgC}, and the anisotropic contribution coming from the spin−spin coupling, J^{aniso}_{HgC}, are presented in Table 4.

As can be seen, the anisotropy of the spin−spin coupling constitutes a large part of the experimentally observable anisotropic coupling D^{exp}_{HgC}, forcing to take it into account were the couplings used for analysis of, for example, the geometry refinement or the orientation parameter.

TABLE 5: ^{199}Hg−^{13}C Spin−Spin Coupling Tensor Isotropies and Anisotropies of Methylmercury Compounds MeHg*X*, X = Me, Cl, Br, I (in Hz) as Derived from Experiments and ZORA Spin−Orbit Relativistic DFT Calculations[a]

molecule	exptl J_{HgC}	calcd J_{HgC}	exptl ΔJ_{HgC}	calcd ΔJ_{HgC}	exptl $(\Delta J/J)_{HgC}$	calcd $(\Delta J/J)_{HgC}$
MeHgCl	1450	1261.0	1160	1224.4	0.80	0.97
MeHgBr	1420	1261.9	1000	1235.9	0.71	0.98
MeHgI	1340	1184.3	980	1225.1	0.73	1.03
MeHgMe	693.8[b]	590.04[d]	855[c]	817.37[d]	1.23	1.38

[a] Computations included 3 DMSO molecules in order to simulate solvent effects, as in Ref 20. For gas-phase data, see text. [b] From ref 11. [c] From ref 9. The given value was obtained in the Merck Phase 4 LC which was used in the other cases as well. [d] Average of the two calculated coupling constants

In Table 5 are collected the experimental and the calculated results for the isotropic average and the anisotropy of the ^{199}Hg−^{13}C spin−spin coupling tensor in the three cases studied. Furthermore, the relative anisotropies, $\Delta J_{HgC}/J_{HgC}$, are given. The relative error limits of the experimental anisotropies of the spin−spin couplings are fairly large (17−27%) and arise almost solely from the uncertainty of the extrapolated isotropic spin−spin coupling constants. If the temperature effects on the isotropic spin−spin coupling constants were ignored and the values obtained from the isotropic phase used (as is done in most studies), the relative error on the anisotropy of the coupling would diminish to a spuriously small value of less than 1%. However, the values of ΔJ_{HgC} obtained this way would deviate from the current result by several percent (7−14%), so that the current, and the more accurate, result would not even fall within the apparent precision. Thus, the more correct analysis leads to seemingly much larger error limits, as it often happens. In principle, the problem with the extrapolation error could be overcome with suitable equipment such as variable angle spinning (VAS) probe, enabling the measurement of the isotropic spin−spin coupling constant at the exactly same circumstances as the anisotropic properties, but the low solubility of the methylmercury halides sets limits to the usefulness of such methods as in standard VAS probes the sample volume is too small to obtain an adequate NMR signal. The error analysis excludes the errors arising from the uncertainty of the r_{α} geometry, and this might have an effect on the results presented, although the adopted geometries have been determined in the same liquid crystal, Phase 4, as used in this study. Unlike the calculated values listed in Table 5, the experimental spin−spin coupling tensors also include rovibrational effects, as the vibrational corrections were only performed on the direct dipolar couplings. The errors arising from the uncertainty of the geometry and the rovibrational effects are in any case small compared to the aforementioned extrapolation error. For the Hg complexes in gas phase, we have calculated intrinsic vibrational corrections on J(Hg−C) of HgMeX at 300 K as 53.6, 53.4, and 52.2 Hz for X = Cl, Br, I, respectively, using the computational methods described in ref 25. The corresponding vibrational corrections to ΔJ(Hg−C) are 27.3, 26.2, and 28.2 Hz. Although the positive vibrational correction on J helps to improve the agreement with experiment, there is no clear trend. For ΔJ, the positive vibrational correction leads to a slight overcorrection of the already too large computed anisotropies, again without a clear trend. The lack of a clear trend can be expected for a vibrational correction that results from the vibration of the light methyl moiety against the much heavier Hg−X unit. The vibrational corrections are small compared to the magnitude of J and ΔJ. At present, it is not clear why the computations do not exhibit the same trend in ΔJ as the experimental data. It is conceivable that a more refined modeling of the LC environment of the Hg systems is necessary to reproduce the trend. Overall, when taking the experimental error bars and typical deviations between theory and experiment of 10−15% for J for the type of computations as performed here[22] into consideration, the NMR measurements and the computational results agree quite well.

Solvent effects were, to a certain extent, studied by repeating the experiments done for CH_3HgCl in Phase 4 for the same molecule but using the liquid crystalline solvent ZLI1982. The final result for the anisotropy of the spin−spin coupling, ΔJ_{HgC} (1140 Hz) deviates less than 2% from the value obtained from Phase 4, thus falling well within experimental error limits and giving no definite indication whether the choice of the liquid crystal used as a solvent has an effect on the results.

For the present work, we have calculated gas-phase isotropic couplings as 811.7, 811.6, 757.6, and 309.0 Hz for HgMeX (X = Cl, Br, I) and $HgMe_2$, respectively. Therefore, the computational results clearly indicate that solvation influences the isotropic coupling significantly, which is in agreement with previous findings.[14,20] Spin−orbit effects which were consistently included here in all computations (except where explicitly noted otherwise), lower the magnitude of the coupling constants. This lowering counterbalances some of the increase in J due to the solvent coordination. We tentatively attribute most of the remaining deviations between theory and experiment to an incomplete treatment of solvent effects.[22]

The gas-phase J-coupling *anisotropies* calculated in this work are 1023.92, 1037.71, 1025.73, and 788.2 Hz for HgMeX (X = Cl, Br, I) and $HgMe_2$, respectively. By comparison with the computational data listed in Table 5, which were obtained with solvent molecules included in the optimized structures, as well as by comparison with experiment it is seen that, due to the presence of solvent, the Hg−C coupling anisotropy is also increased by solvent coordination, by about 20%. For MeHgCl, this brings the coupling anisotropy closer to the experimental value, but for MeHgI, the deviation between computations and experiment increases because the computed anisotropies do not exhibit a similarly pronounced trend as the experimental ones. The relative change in the anisotropies resulting from coordination of Hg by the solvent is seen to be considerably smaller than the change in the isotropic J-couplings, i.e., the solvent mainly affects the isotropic FC coupling mechanism. Due to the underestimation of the calculated isotropic couplings, the relative anisotropies are larger in the computations. The difference between the MeHgX and the MeHgMe systems is clearly reflected by the theoretical data, with a MeHgMe/MeHgX ratio of the relative anisotropies on the order of 1.4. Given the experimental error bars and approximation in the computations, this ratio compares reasonably well with the experimental ratios of 1.5 to 1.7.

From the computational data, is it possible to determine which of the J-coupling mechanisms is responsible for the large relative anisotropies. Taking Me−Hg−Cl as an example, a calculation similar to those of Table 5 but *excluding* spin−orbit coupling yields J = 1335.9 and ΔJ = 1096.1 Hz, i.e., J is larger in magnitude compared to the spin−orbit computations, while ΔJ is noticeably smaller. Therefore, we can confirm the finding of Pyykkö[19] which was based on a semiempirical calculation that spin−orbit coupling increases the relative anisotropy of the Hg−C coupling tensor. We find the same trends for the other systems as well, including Me−Hg−Me. As already mentioned, spin−orbit coupling tends to reduce the magnitude of the isotropic J for these systems, which has previously been assigned to contributions from a FC−PSO spin−orbit cross term.[14,20] Here, we find that this term is also responsible for most of the difference in ΔJ when comparing spin−orbit and spin-free relativistic results. In the spin-free relativistic calculations, the PSO mechanism is almost negligible (the tensor elements are smaller than 10 Hz in magnitude), while an anisotropy of about 1.0 and 0.6 kHz remains for the Me−Hg−X systems and for Me−Hg−Me, respectively. Therefore, most of the anisotropy of the Hg−C coupling tensor is attributable to the FC−SD spin mechanism. This mechanism includes a cross term involving both the FC and the SD operators. Because the matrix elements for the FC operator are significantly larger when solvent molecules are coordinated to the metal, it is clear why the anisotropy is also affected by the presence of solvent molecules and why it is larger in solution than in gas phase.

Conclusions

The proton decoupled ^{13}C NMR spectra with ^{199}Hg satellites of methylmercury halides, MeHgX (X = Cl, Br, I), revealed the quantity $|2D_{HgC} + J_{HgC}|$ with good precision. However, to get this quantity, one had to carry out very demanding experiments from the sensitivity point of view: First, the solubility of the compounds into liquid crystals is very low. Second, the number of isotopomers with both ^{13}C and ^{199}Hg isotopes is very small, only about 0.18%. The D_{HgC} values were derived for each compound using extrapolated J values. The D values include a sizable contribution from the anisotropy of the respective spin−spin coupling tensor, $(^1/_2)J^{aniso}_{HgC}$. This, together with the orientational order parameter of the molecular symmetry axis, obtained from the experimental D_{CH} couplings, made feasible the determination of the anisotropy, ΔJ_{HgC}, of the $^{13}C-^{199}Hg$ spin−spin coupling tensor. Experiments reveal a trend in the order: ΔJ_{HgC}(MeHgCl) > ΔJ_{HgC}(MeHgBr) > ΔJ_{HgC}(MeHgI) > ΔJ_{HgC}(MeHgMe). The computations reproduce the difference between Me−Hg−Me and Me−Hg−X very clearly but do not show a clear trend among the Me−Hg−X systems. It is yet unclear if this is a discrepancy between theory and experiment that might be due to the computational modeling of solvent−solute interaction. Considering the experimental error bars, and the approximate nature of the computations, good agreement is found between the experimental and the calculated ΔJ_{HgC} as long as solvent effects are considered in the computations. Most of ΔJ can be attributed to the spin mechanism of J-coupling, with additional sizable spin−orbital FC−PSO cross terms due to electronic spin−orbit coupling. Solvent effects were shown to increase the magnitude of ΔJ, but to a lesser extent than what is obtained for the isotropic coupling.

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