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Zero-Point Vibrational Effects on Proton Shieldings: Functional-Group Contributions from ab Initio Calculations

Kenneth Ruud,*,† Per-Olof Åstrand,‡ and Peter R. Taylor†

Contribution from the San Diego Supercomputer Center and Department of Chemistry and Biochemistry, University of California, San Diego, 9500 Gilman Drive MC0505, La Jolla, California 92093-0505, and Materials Research Department, Risø National Laboratory, POB 49, DK-4000 Roskilde, Denmark

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Abstract: We investigate the effects of zero-point vibrational motion on the nuclear magnetic shielding constants of a large number of organic molecules. The vibrational corrections include anharmonic contributions from the potential energy surface and harmonic contributions from the curvature of the property surface. Particular attention is paid to vibrational corrections to hydrogen shielding constants where we show that vibrational corrections may be substantial, ranging from about +0.50 to −0.70 ppm, and thus demonstrating that ignoring these effects may give errors in the *chemical shifts* by more than 1 ppm in certain extreme cases. These effects can therefore not be neglected when comparing calculated results with experiment, not even for the chemical shifts. However, we also demonstrate that the vibrational corrections to the hydrogen shieldings are to a large extent transferable from one molecule to another. We have tabulated functional vibrational corrections to the hydrogen shieldings, based on results for more than 35 molecules. Unfortunately, no similar transferability has been observed for the vibrational corrections to shielding constants of other nuclei such as carbon, nitrogen, or oxygen.

I. Introduction

Today, nuclear magnetic resonance (NMR) is one of the most important spectroscopic tools for characterization of molecules.[1] Given the abundance of hydrogens in most organic molecules, much of its success has been due to the ease with which one can analyze, in particular, proton NMR spectra through various "rules-of-thumb" for the chemical shifts of hydrogens belonging to different types of functional groups.[2,3] The success of these rules-of-thumb is somewhat surprising, considering the fact that the nuclear magnetic shielding is a most sensitive probe of the molecular electronic structure in the vicinity of the nucleus, as exemplified by NMR's utility as an important tool for investigating intra, intermolecular, and solvent effects because of the way these perturb the shielding constants in a molecule.[4] For larger molecules, decoupling the effect of external (or internal) perturbations on the large number of nuclei available to NMR investigation may be difficult. Significant advances here have been achieved experimentally through high-field NMR instruments, but at the expense of introducing additional observable magnetic-field dependence into the nuclear shielding and spin−spin coupling constants.[5,6] An alternative approach is to combine experimental observations with theoretical calculations. This approach was not explored to any large extent until the beginning of the 1990s (although important work was presented by Kutzelnigg and co-workers already in the mid-1980s[7,8]) due to problems with gauge-origin dependence in approximate wave function calculations.[9,10] In 1990 Wolinski, Hinton, and Pulay presented the first efficient implementation for calculating nuclear magnetic shielding constants using London atomic orbitals and analytical derivatives,[11] and the field of theoretical calculations of NMR parameters has grown steadily ever since, with several recent meetings and reviews being devoted to the topic of theoretical predictions of NMR parameters.[10,12−18,] Gauge-origin independent approaches for calculating shielding constants have now been presented for almost any correlated wave function,[19−25] as have approaches for treating large molecular systems.[26−28]

The main focus of most of these developments has been on the electronic contributions to the shielding constants and

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* Corresponding author. Present address: Department of Chemistry, University of Tromsø, N-9037 Tromsø, Norway.

† University of California.

‡ Risø National Laboratory.

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accurate treatments of the electron correlation effects. On the other hand, studies on small molecules have demonstrated that the effects of nuclear motion may be as important as electron correlation for a detailed comparison with experiment.[29−33] In many cases, vibrational corrections may even be as large as the correlation effect itself, a striking example being the nitrogen shielding constant in ammonia:[32] at the Hartree−Fock level, the nitrogen shielding constant is 262 ppm. Electron correlation (at the MCSCF level) increases the shielding to 274 ppm (although probably slightly overestimating the correlation effect), and zero-point vibrational corrections then reduce it to 267 ppm. The experimental result is 264.5 ppm, and it would thus appear that the Hartree−Fock approach performs better than the correlated approximation if vibrational effects are neglected. Even though this is misleading, including electron correlation without taking into account zero-point vibrations may give an incorrect impression of the accuracy of the calculated value as compared to experimental nuclear shieldings. We recently presented a method for calculating vibrational corrections to molecular properties in which the vibrational wave function was considered to be a product of simple harmonic oscillators.[34,35] The anharmonic contributions were included by shifting the molecular geometry from an equilibrium geometry to an *effective geometry* where the main anharmonic contributions to the vibrational average vanishes. It could also be shown that this effective geometry is, to second-order in perturbation theory, identical to the vibrationally averaged geometry. We applied our approach for accurate calculations of zero-point vibrational corrections to a range of molecular properties for the 10-electron hydride series HF, H_2O, NH_3, and CH_4.[32] An interesting observation was that the vibrational corrections to the hydrogen shieldings seemed to be independent of electron correlation. This lack of electron correlation effect on the hydrogen shieldings has also been observed by Chesnut for a different set of molecules.[33] It was also noted in this work that the hydrogen shieldings were quite sensitive to the size of the one-particle basis set as well as the importance of rovibrational corrections. Another interesting observation for the hydrogen shielding in the 10-electron hydrides was that the vibrational corrections themselves seemed to be almost identical for all four molecules.[32] Since the corrections were large, about −0.60 ppm, and significantly larger than any electron correlation contribution, it would clearly be of interest to investigate if it is possible to find a set of transferable parameters for the vibrational corrections to hydrogen shielding constants, in much the same way as Pascal's rule uses transferable atomic magnetizabilities for calculating molecular diamagnetic susceptibilities.[36] In this work we explore this possibility by calculating zero-point vibrational corrections to the nuclear shielding constants of 38 organic molecules, ranging in size from methane to benzoic acid. The rest of the paper is divided into four major sections. In section II we briefly summarize our approach for calculating zero-point vibrational corrections to molecular properties. Section III summarizes the computational details for the calculations. In section IV we discuss our results. However, because of the large amount of calculated data, focus will be on general trends and observations.Section IVA will discuss in some more detail the results obtained for aromatic systems, since these systems clearly demonstrate the transferability, as well as the limitation of this transferability to the *vibrational* contributions to the hydrogen shielding constants. In section IVB we present our suggested vibrational corrections to theoretically calculated nuclear shielding constants, before comparing these predictions with experimental observations. Finally, in section V we discuss the implications of our work for future theoretical studies of nuclear shieldings and give some concluding remarks.

II. The Molecular Vibrational Wave Function

We will not discuss our method for calculating the zero-point vibrational corrections to the nuclear shieldings in detail, as the theory has been discussed extensively in several previous papers.[32,34,35] However, for completeness we give a brief overview of our approach, since it differs from the methods usually applied to the calculation of zero-point vibrational effects on properties, and some parts of our later discussion will also require a basic understanding of the method.

Our basic ansatz is to determine an effective geometry, r_{eff}, in a variational approach by minimizing the energy functional[37]

$$\tilde{E}^{(0)} = V^{(0)}_{\mathrm{exp}} + \frac{1}{2}\sum_{i=1}^{N}\omega_{\mathrm{exp},i} \qquad (1)$$

with respect to the expansion point, r_{exp}. Here $V^{(0)}_{\mathrm{exp}}$ is the potential energy and $\omega_{\mathrm{exp},i}$ is the harmonic frequency for mode i, both calculated at the expansion point, r_{exp}. N is the number of vibrational modes. The second term on the right-hand side of eq 1 is the zero-point vibrational energy. If a perturbation expansion is carried out around r_{eff} instead of around the equilibrium geometry r_{e}, following the strategy as employed by Kern and Matcha[38] for an expansion around r_{e}, several things are noted.[32,34,35,39] The effective geometry may be determined as

$$r_{\mathrm{eff},j} = r_{\mathrm{e},j} - \frac{1}{4\omega_{e,j}^{2}}\sum_{m=1}^{N}\frac{V^{(3)}_{e,jmm}}{\omega_{e,m}} \qquad (2)$$

where $V^{(3)}$ is the cubic force field, and where we have used mass-weighted coordinates. We note that this geometry corresponds to the vibrationally averaged molecular geometry to second-order in perturbation theory. The reason is that for this choice of expansion point the leading first-order correction to the vibrational wave function vanishes and, consequently, that the leading term to the vibrational average of a molecular property arising from the anharmonicity of the potential is included implicitly by the shift of expansion point. The leading terms in a zero-point vibrationally averaged molecular property $\langle P\rangle$ may thus be obtained as

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$$\langle P\rangle = P_{\rm eff} + \langle P_2^{(0)}\rangle_{\rm eff} = P_{\rm eff} + \frac{1}{4}\sum_{i=1}^{N}\frac{P^{(2)}_{{\rm eff},ii}}{\omega_{{\rm eff},i}} \qquad (3)$$

where $P^{(2)}_{\rm eff}$ is the second derivative of the property surface calculated at $r_{\rm eff}$. The leading term in the vibrational average is thus obtained as a sum of two contributions, where the first is due to the shift of expansion point and the second is a harmonic term obtained from the curvature of the property surface and the harmonic frequencies.

III. Computational Details

All of the results reported here have been obtained with a locally modified version of the Dalton quantum chemistry program,[40] in which the approach for calculating effective molecular geometries and zero-point vibrational averages has been implemented recently.[35,32] For all molecules we have used the valence triple-ζ basis sets developed by Ahlrichs, Horn, and Schäfer,[41] with an extra polarization function for each atom with exponents 0.8 (H/C), 1.0 (N), and 1.2 (O). This basis set has been used extensively in MP2 and CCSD calculations of nuclear shieldings by Gauss and co-workers,[19,20,21,24] and a recent review demonstrates the excellent behavior of this basis set for the calculation of nuclear shielding constants.[10] As our main focus will be on the hydrogen shieldings, for which electron correlation effects seem to be negligible both for the shieldings themselves[33] as well as their vibrational corrections,[32] all calculations reported here have been restricted to the Hartree−Fock level.

We note that our zero-point vibrational corrections have been evaluated using the most abundant isotope for each atom in each molecule. Strictly speaking, therefore, it is not correct to report zero-point vibrational corrections to the shieldings of nuclei such as carbon and oxygen, since the observable isotopes of these atoms are most likely to be ^{13}C and ^{17}O, respectively. However, the error introduced by this approximation is likely to be much smaller than the error introduced by the neglect of electron correlation effects when evaluating the nuclear shielding constants for these heavier atoms, and we can ignore it here.

The geometries of the molecules were optimized using the first-order methods implemented in the Dalton program and described by Bakken and Helgaker.[42] The geometries were verified to be true minima by a calculation of the harmonic force field at this geometry. Effective geometries were obtained according to eq 2. At the effective geometry, translational and rotational forces acting on the molecule due to the use of a nonequilibrium geometry were projected out. In a few cases, imaginary frequencies were obtained at the effective geometry. These imaginary frequencies were in all cases associated with localized internal rotations about one or more bonds, such as rotations of the OH group in some of the alcohols, rotation of the NH_2 group, or rotations of methyl groups. Imaginary frequencies also occurred in previous work where intermolecular vibrations of bimolecular complexes were investigated.[37] It was argued that these low-frequency modes can be decoupled from the other modes in a Born−Oppenheimer-type of approximation and thereby be treated separately. In this work we have also ignored the imaginary frequencies. For some molecules for which one would expect imaginary frequencies to appear on the basis of the criteria just given, they did not occur. An analysis of the normal modes in these instances, such as for instance propyne, shows that the internal rotation is strongly coupled to the vibration of other atoms in the molecule; in this case, the internal rotation of the methyl group is strongly coupled to a simultaneous bending of the acetylenic hydrogen.

Because the molecules for which we obtain imaginary frequencies at the effective geometry have essentially free internal rotations, it may also be argued that this intramolecular motion cannot be treated by a simple perturbation expansion around the effective geometry or equivalently around the equilibrium geometry, but instead should be treated by a full exploration of the potential energy surface associated with the internal rotation. Such an approach would be very time-consuming for the molecules studied here, and we have not pursued this further. However, we note that a recent investigation by Baaden, Granger, and Strich[43] addressed this point. They found that for gaseous and liquid samples, free rotations around single bonds did not change the hydrogen shielding constants of the molecule significantly, the effect in general being much less than 1% of the electronic contribution. For our purpose, we consider the neglect of these imaginary modes to be well justified. As will be seen, even for molecules where imaginary frequencies do occur, the transferability of the zero-point vibrational corrections to the hydrogen shieldings still remains, indicating that the neglected modes do not contribute significantly to the zero-point vibrational corrections.

Table 1. Molecules Studied in This Investigation

class	molecules
hydrocarbons	methane, ethane, propane, cyclopropane, butane, 2-methylpropane, ethene, propene, cyclopropene, allene, 1-butene, *trans*-2-butene, cyclobutane, cyclobutene, butadiene, cyclobutadiene, ethyne, propyne
alcohols	methanol, ethanol, 1-propanol, 2-propanol, 3-hydroxypropene
ketones/aldehydes	formaldehyde, ethanal, propanal, cyclopropanone
etheres	dimethyl ether, oxirane
acids	formic acid, propanoic acid
amines	ethanamine, 1-propanamine, 2-propanamine
aromatics	benzene, phenol, aniline, toluene, benzoic acid

Table 2. Contributions to the Isotropic Shielding Constants of **Methane** as Obtained at the Hartree−Fock Level[a]

	$\sigma_{\rm e}$	$\sigma_{\rm eff}$	$\sigma_{\rm eff} - \sigma_{\rm e}$	$\langle\sigma_2^{(0)}\rangle$	$\langle\sigma\rangle_{\rm ZPV}$	$\langle\sigma\rangle$
$\sigma^{\rm C}$	197.83	195.29	−2.54	−0.66	−3.20	194.63
$\sigma^{\rm H}$	31.96	31.54	−0.42	−0.17	−0.59	31.37

[a] All shielding constants reported in ppm. $\sigma_{\rm e}$ and $\sigma_{\rm eff}$ are the shieldings at the equilibrium and effective geometry, respective. $\langle\sigma_2^{(0)}\rangle$ is defined in eq 3, $\langle\sigma\rangle$ is the vibrationally averaged shielding and $\langle\sigma\rangle_{\rm ZPV}$ is the difference between $\langle\sigma\rangle$ and $\sigma_{\rm e}$. Equilibrium bond length is 108.30 pm, and the bond length at the effective geometry is 109.51 pm.

All optimized and effective geometries (in Cartesian coordinates) are available as Supporting Information, as are all calculated shielding constants and corresponding zero-point vibrational corrections.

IV. Results

Shielding constants and their vibrational corrections have been calculated for a total of 38 molecules, and these molecules are listed in Table 1.

We will not discuss all of the results but focus on a few particular systems. We will start our discussion with the simplest example, namely methane, for which our results are collected in Table 2. For this molecule, we may also compare the results with our previous calculations including electron correlation.[32] It is observed that the zero-point vibrational correction to the hydrogen shielding is sizable, −0.59 ppm, and compares favorably with our correlated result of −0.60 ppm.[32] Interestingly, our zero-point vibrational correction to the carbon shielding is identical to our MCSCF correction in ref 32, −3.20 ppm. However, this is undoubtedly a basis set effect, as the Hartree−Fock result in ref 32 is −3.07 ppm. Although this result may seem to imply that also carbon shieldings and their vibrational corrections may be correlation-independent, there is ample evidence for the contrary.[10]

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Table 3. Contributions to the Isotropic Shielding Constants of **Propane** as Obtained at the Hartree−Fock Level[a]

	σ_e	σ_{eff}	$\sigma_{eff} - \sigma_e$	$\langle\sigma_2^{(0)}\rangle$	$\langle\sigma\rangle_{ZPV}$	$\langle\sigma\rangle$
σ^{C_m}	177.84	176.11	−1.73	−3.49	−5.22	172.62
σ^{C}	178.65	178.41	−0.24	−4.02	−4.26	174.39
$\sigma^{H_{ip}}$	31.34	31.34	0.00	−0.67	−0.67	30.67
$\sigma^{H_{op}}$	31.60	31.56	−0.04	−0.66	−0.70	30.90
σ^{H_m}	31.21	30.98	−0.23	−0.47	−0.70	30.51

[a] All shielding constants reported in ppm. For a definition of all quantities, see Table 2.

There have been several discussions in the literature as to whether MP2 optimized geometries or experimental geometries are the best structures to use in calculations of nuclear shielding constants.[44,11] It is clear from the discussion in section II that the effective geometry corresponds, to a very good approximation, to the vibrationally averaged molecular geometry. It can therefore be argued that by using the experimental geometry one may indirectly recover some of the vibrational corrections, namely the most important contribution arising from the anharmonicity of the potential surface.[33] Thus, if this term dominates the vibrational corrections, most of the vibrational effects would implicitly be accounted for by using experimental r_0 geometries. The results for methane would seem to validate such an approach, since the shift in the geometry accounts for about 70% of the vibrational correction for both the carbon and the hydrogen shielding constants.

It is then instructive to consider a closely related molecular system, namely propane, and the results for propane are collected in Table 3. For all shieldings in this molecule, the shift in geometry gives a significantly smaller contribution to the zero-point vibrational corrections than that arising from the harmonic term in eq 3. More importantly, calculating the shielding at the effective geometry while not accounting for the harmonic term would change the relative chemical shifts of the protons on the middle carbon relative to the terminal protons. This is due to the fact that the former has a sizable contribution from the shift of expansion point, whereas this contribution to the latter is negligible. The difference would be even more dramatic if we tabulated the relative chemical shifts of propane to those of methane, where errors in the chemical shifts of 0.40 ppm would be introduced if the harmonic term had not been included. For these structurally related protons, it would actually be more advantageous to use optimized molecular structures and ignore zero-point vibrational effects altogether when estimating relative chemical shifts, as we will return to in section IVB. It is interesting to observe the transferability of the zero-point vibrational corrections despite the fact that the relative contributions to the zero-point corrections of the two terms vary considerably. Possibly there may exist an alternative representation of the vibrational wave function that would be more suitable for the calculation of vibrational corrections to hydrogen shieldings.

We also discuss briefly an example involving a strongly polar group, choosing for simplicity methanol. The results for this molecule are collected in Table 4. Considering the very different electronic distribution in methane compared to that in methanol, because of the polarity of the hydroxy group, it is remarkable that the zero-point vibrational corrections to the methyl protons in methanol are basically identical to those in methane, whereas the electronic counterpart becomes less shielded by almost 3 ppm. We will see that this is a unique feature of the zero-point vibrational corrections to the hydrogen shieldings. The vibrational corrections to the carbon shielding are also remarkably unaffected by the exchange of a hydrogen with a hydroxy group (3.20 ppm in methane and 3.44 ppm in methanol). The zero-point vibrational corrections are fairly large for all nuclei, although not relative to the electronic contribution, the vibrational corrections being less than 2% for all shieldings. We note that the corrections to the oxygen shielding are rather small for this molecule, in part because the zero-point vibrational correction itself is small, but this is further accentuated by the large electronic contribution. This situation can be contrasted with, for instance, the case of benzoic acid (vide infra).

For methanol, we also note that the difference in the zero-point vibrational corrections for the methyl protons and the hydroxy proton are large, being −0.60 ppm and 0.26 ppm, respectively. Thus if one considers only the electronic contribution to the shielding, the error even in the internal chemical shifts in methanol will be almost 0.90 ppm, that is, *10% of the entire chemical shielding range of protons*. Clearly, for molecules containing such polar groups zero-point vibrational corrections cannot be neglected. However, it is important to realize that this result applies to results in the gas phase, and in a comparison with experimental chemical shifts obtained in the liquid phase, the observed chemical shifts are likely to be strongly modified by the solvent, in particular if the proton of interest can be involved in hydrogen bonding. It should also be noted that the potential surface of an alcohol is strongly modified in the neat liquid, which is realized from the equilibrium $-OH \rightleftharpoons -O^- + H^+$ occurring in the liquid phase. It would clearly be of interest to investigate in more detail the effects of hydrogen bonding in the liquid phase on both the electronic[45,46] and the zero-point vibrational contributions to the hydrogen chemical shifts.

A. The Aromatic Molecules. We will discuss in some additional detail the aromatic molecules included in this study: benzene, toluene, aniline, phenol, and benzoic acid. These molecules clearly demonstrate the transferability of the vibrational corrections to the hydrogen shieldings for hydrogens belonging to similar functional groups, and equally clearly demonstrate the lack of such transferability for the vibrational corrections to the carbon shielding constants, as well as for the electronic contribution to both the hydrogen and carbon shieldings.

The results for benzene, toluene, aniline, phenol, and benzoic acid are collected in Tables 5−9. We will in this discussion ignore all atoms except the aromatic carbon atoms and the hydrogen atoms directly attached to the phenyl ring. We note that for all molecules, the vibrational corrections to the hydrogen shieldings are almost independent of their position (*ortho*-, *meta*-, or *para*-) relative to the functional group. This observation is in marked contrast to the electronic contributions to the hydrogen shieldings, for which the position of the hydrogen relative to the functional group is clearly reflected in the nuclear shielding. It is also interesting to note that the zero-point vibrational corrections are more or less independent of the functional group attached to the phenyl ring, and thus the different vibrational modes associated with the different functional groups do not affect the vibrational corrections to the aromatic hydrogens. We note, however, that, although the differences are small, the benzene molecule gives rise to zero-point vibrational corrections slightly different from those of the other aromatic molecules.

In marked contrast, the zero-point vibrational corrections to the carbon shieldings in the phenyl group depend strongly on

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Table 4. Contributions to the Isotropic Shielding Constants of **Methanol** as Obtained at the Hartree−Fock Level[a]

	σ_e	σ_{eff}	$\sigma_{eff} - \sigma_e$	$\langle\sigma_2^{(0)}\rangle$	$\langle\sigma\rangle_{ZPV}$	$\langle\sigma\rangle$
σ^{C}	148.60	147.07	−1.53	−1.91	−3.44	145.16
σ^{O}	348.35	350.97	2.62	−7.13	−4.52	343.83
$\sigma^{H1(2)/3}$	29.35/29.22	29.09/28.96	−0.26/−0.26	−0.35/−0.35	−0.60/−0.61	28.75/28.61
σ^{H4}	32.96	33.45	0.49	−0.24	0.26	33.22

[a] All shielding constants reported in ppm. For a definition of all quantities, see Table 2.

Table 5. Contributions to the Isotropic Shielding Constants of **Benzene** as Obtained at the Hartree−Fock Level[a]

	σ_e	σ_{eff}	$\sigma_{eff} - \sigma_e$	$\langle\sigma_2^{(0)}\rangle$	$\langle\sigma\rangle_{ZPV}$	$\langle\sigma\rangle$
σ^{C}	59.46	58.16	−1.30	−2.07	−3.37	56.09
σ^{H}	24.81	24.69	−0.12	−0.26	−0.38	24.42

[a] All shielding constants reported in ppm. For a definition of all quantities, see Table 2.

Table 6. Contributions to the Isotropic Shielding Constants of **Toluene** as Obtained at the Hartree−Fock Level[a]

	σ_e	σ_{eff}	$\sigma_{eff} - \sigma_e$	$\langle\sigma_2^{(0)}\rangle$	$\langle\sigma\rangle_{ZPV}$	$\langle\sigma\rangle$
σ^{C}	174.67	173.15	−1.52	−4.68	−6.19	168.48
σ_i^{C}	48.01	46.64	−1.37	−2.40	−3.77	44.24
σ_o^{C}	59.89	58.67	−1.22	−1.74	−2.96	56.93
σ_m^{C}	58.71	57.51	−1.20	−3.12	−4.34	54.39
σ_p^{C}	63.21	61.98	−1.23	−3.71	−4.94	58.27
σ_o^{H}	24.96	24.84	−0.12	−0.27	−0.40	24.56
σ_m^{H}	24.91	24.79	−0.12	−0.27	−0.39	24.52
σ_p^{H}	25.06	24.95	−0.11	−0.34	−0.45	24.61
σ^{H}	29.84	29.58	−0.26	−0.63	−0.89	28.95
σ_2^{H}	30.18	29.92	−0.26	−0.61	−0.87	29.31

[a] All shielding constants reported in ppm. For a definition of all quantities, see Table 2.

Table 7. Contributions to the Isotropic Shielding Constants of **Aniline** as Obtained at the Hartree−Fock Level[a]

	σ_e	σ_{eff}	$\sigma_{eff} - \sigma_e$	$\langle\sigma_2^{(0)}\rangle$	$\langle\sigma\rangle_{ZPV}$	$\langle\sigma\rangle$
σ_i^{C}	36.66	35.70	−0.96	−3.35	−4.30	32.36
σ_o^{C}	77.12	76.45	−0.67	−3.72	−4.40	72.72
σ_m^{C}	54.99	53.69	−1.30	−2.75	−4.04	50.95
σ_p^{C}	72.63	71.73	−0.90	−2.64	−3.53	69.10
σ^{N}	212.82	216.38	3.56	−8.35	−4.79	208.03
σ_o^{H}	25.61	25.52	−0.09	−0.32	−0.41	25.21
σ_m^{H}	24.94	24.82	−0.12	−0.31	−0.43	24.51
σ_p^{H}	25.60	25.51	−0.09	−0.34	−0.43	25.17
σ_N^{H}	29.63	30.02	0.39	−0.55	−0.16	29.47

[a] All shielding constants reported in ppm. For a definition of all quantities, see Table 2.

Table 8. Contributions to the Isotropic Shielding Constants of **Phenol** as Obtained at the Hartree−Fock Level[a]

	σ_e	σ_{eff}	$\sigma_{eff} - \sigma_e$	$\langle\sigma_2^{(0)}\rangle$	$\langle\sigma\rangle_{ZPV}$	$\langle\sigma\rangle$
σ_i^{C}	30.33	29.43	−0.90	−3.06	−3.96	26.38
σ_p^{C}	70.40	69.00	−1.40	−2.94	−4.34	64.66
σ_o^{C}	79.06	77.73	−1.33	−3.27	−4.60	74.46
σ_o^{C}	74.42	73.14	−1.28	−3.06	−4.34	70.08
σ_m^{C}	54.53	53.39	−1.14	−3.16	−4.30	50.23
σ_m^{C}	55.88	54.73	−1.15	−2.92	−4.06	51.82
σ^{O}	251.80	257.85	6.05	−9.41	−3.36	248.44
σ_o^{H}	25.80	25.66	−0.14	−0.26	−0.40	25.40
σ_o^{H}	25.20	25.11	−0.09	−0.32	−0.41	24.80
σ_m^{H}	24.82	24.70	−0.12	−0.34	−0.45	24.37
σ_m^{H}	24.93	24.81	−0.12	−0.31	−0.43	24.50
σ_p^{H}	25.43	25.32	−0.11	−0.33	−0.45	24.98
σ_O^{H}	28.91	29.70	0.80	−0.22	0.58	29.49

[a] All shielding constants reported in ppm. For a definition of all quantities, see Table 2.

Table 9. Contributions to the Isotropic Shielding Constants of **Benzoic Acid** as Obtained at the Hartree−Fock Level[a]

	σ_e	σ_{eff}	$\sigma_{eff} - \sigma_e$	$\langle\sigma_2^{(0)}\rangle$	$\langle\sigma\rangle_{ZPV}$	$\langle\sigma\rangle$
σ^{C1}	25.50	25.61	0.11	−12.45	−12.34	13.05
σ^{C2}	61.34	60.10	−1.24	2.01	0.77	62.11
σ^{C3}	52.26	51.24	−1.02	0.86	−0.16	51.08
σ^{C4}	53.22	52.21	−1.01	0.13	−0.88	52.34
σ^{C5}	54.97	53.90	−1.07	1.94	0.87	54.77
σ^{C6}	62.62	61.54	−1.08	0.76	−0.32	62.30
σ^{C7}	62.00	60.95	−1.05	0.31	−0.74	61.26
σ^{O1}	−39.71	−41.56	−1.85	−31.24	−33.09	−72.80
σ^{O2}	177.43	179.42	1.99	−17.99	−16.00	161.43
σ^{H1}	23.71	23.62	−0.09	−0.28	−0.37	23.34
σ^{H2}	23.96	23.86	−0.10	−0.03	−0.13	23.83
σ^{H3}	24.87	24.77	−0.10	−0.30	−0.40	24.47
σ^{H4}	24.81	24.71	−0.10	−0.24	−0.34	24.47
σ^{H5}	24.54	24.44	−0.10	−0.32	−0.42	24.12
σ^{H6}	26.84	27.09	0.25	−0.81	−0.56	26.28

[a] All shielding constants reported in ppm. For a definition of all quantities, see Table 2.

the position of the carbon relative to the functional group, as do their electronic contributions. Another interesting observation is that, in contrast to the hydrogen shieldings, the magnitude of zero-point vibrational corrections to the carbon atoms may both increase and decrease with increasing distance to the functional group, depending on the nature of the substituent (ignoring the *ipso*-carbon). In toluene, for example, the ZPV corrections increase from the *ortho*- to the *para*-position (see Table 6), whereas the ZPV corrections decrease from the *ortho*- to the *para*-position in aniline (see Table 7).

Thus, for this class of structurally similar molecules, the unique nature and transferability of the zero-point vibrational corrections to hydrogen shieldings are clearly displayed. This class of molecules also provides ample evidence that similar transferability does not appear to be possible for the zero-point vibrational corrections to the nuclei other than hydrogen investigated here unless of course a much more fine-grained partitioning of the nuclei into chemically equivalent sets is used. Although it may be argued that for the non-hydrogen shieldings, the Hartree−Fock approximation may not be sufficient, we find it unlikely that electron correlation will introduce any sort of transferability in the zero-point vibrational corrections for the heavier nuclei that is absent at the Hartree−Fock level. In the rest of this section we will therefore focus our attention on the zero-point vibrational corrections to the hydrogen shieldings and present rules-of-thumb corrections to calculated electronic hydrogen shieldings.

We would also like to draw attention to the zero-point vibrational corrections to the oxygen shielding in phenol and in benzoic acid. As was the case for methanol, the zero-point vibrational correction to the oxygen atom in the hydroxyl-group is of very minor importance compared to the electronic contribution. In marked contrast to this we find the zero-point vibrational contribution to the carbonyl oxygen in benzoic acid to be almost as large as the electronic contribution itself, leading

Table 10. Functional Zero-Point Vibrational Contributions to the Hydrogen Shielding Constants

methane	−0.59
$-CR_2H$	−0.70 ± 0.11
$=CRH$	−0.46 ± 0.13
$\equiv CH$	−0.76 ± 0.01
H−CRO	−0.55 ± 0.06
RO−H	0.48 ± 0.13
$RN-H_2$	−0.18 ± 0.03
RCOO−H	−0.49 ± 0.06
Ar−H	−0.39 ± 0.06

to an overall doubling of the ^{17}O shielding constant when zero-point vibration effects are included. Similar observations can made for the other carbonyl oxygen in the acids, aldehydes, and ketones investigated here. These findings are in marked contrast to what have been observed as ZPVC to oxygen shieldings for small molecules, where accurate calculations find a quite substantial ZPVC to the single-bonded oxygen shielding in water,[47] and a rather modest ZPVC to the double-bonded oxygen shielding in CO.[48]

B. Vibrational Corrections to Hydrogen Shielding Constants. As we have indicated in previous sections, the zero-point vibrational corrections to the hydrogen shielding constants display a remarkable degree of transferability for all of the molecules we have investigated, as can be seen from Tables 2−9 as well as from the data provided in the Supporting Information. We have analyzed the data and carried out a statistical analysis of the zero-point vibrational corrections to these proton shieldings grouped according to their functional nature. The final data are collected in Table 10. We believe that these data will provide a simple approximation to the vibrational corrections to hydrogen shieldings in almost any kind of organic molecule. We note that the standard deviations are fairly modest, indicating that these correction factors should indeed prove useful in correcting theoretically calculated electronic hydrogen shieldings, hopefully also improving the agreement with experiment (vide infra). We also note here that the median values for all shieldings are more or less coincident with the average values reported in Table 10, the largest difference appearing for the hydroxy proton, the median being 0.56 ppm, as compared to the average value of 0.52 ppm.

Considering the transferability of the zero-point vibrational corrections to the hydrogen shielding constants of a given functional group in structurally very different molecules, it is relevant to ask if this transferability arises because the zero-point vibrational corrections to the hydrogen shieldings receive most of their magnitude from vibrations in the vicinity of the hydrogen atom in question. An analysis of this is difficult because it is hard to isolate which changes in the geometry are the most important for the shielding when going from the equilibrium to the effective geometry. In Table 11 we have collected the contributions to the zero-point corrections from the harmonic term for the different vibrational modes in ethane, $\langle\sigma_2^{(0)}\rangle$. This term dominates the zero-point vibrational corrections in ethane and may therefore shed some light on this question. We observe that both for the carbon and the hydrogen shielding, most vibrational modes contribute significantly to the total $\langle\sigma_2^{(0)}\rangle$ term. The results in Table 11 also indicate that it may prove difficult to devise a strategy for isolating important vibrational modes, as has been done for pure vibrational effects to molecular (hyper)polarizabilities.[49,50] In fact, such an approach may do more harm than good because it risks including terms that would be partially canceled by other vibrational modes in the molecule.

Table 11. Vibrational Frequencies, Second-Derivatives of the Nuclear Shieldings and Contribution to the $\langle\sigma_2^{(0)}\rangle$ Term from the Different Vibration Modes in Ethane[a]

		$\partial^2\sigma k/\partial Q_i^2$		$\langle\sigma_2^{(0)}\rangle_i$	
mode no.	frequency	C	H	C	H
1	3178.72	−31.63	4.64	−0.30	0.04
2	3178.72	−31.62	−1.41	−0.30	−0.01
3	3152.42	−31.46	4.47	−0.30	0.04
4	3152.41	−31.48	−1.44	−0.30	−0.01
5	3116.39	−9.73	3.47	−0.09	0.03
6	3109.98	−15.67	3.11	−0.15	0.03
7	1625.76	1.55	−1.12	0.03	−0.02
8	1625.76	1.55	−4.21	0.03	−0.08
9	1622.01	−4.46	−1.77	−0.08	−0.03
10	1622.01	−4.46	−3.80	−0.08	−0.07
11	1559.06	2.51	−2.09	0.05	−0.04
12	1529.73	6.92	−1.89	0.14	−0.04
13	1322.28	3.81	−2.71	0.09	−0.06
14	1322.28	3.81	−0.41	0.09	−0.01
15	1021.55	−6.56	−0.43	−0.19	−0.01
16	903.15	−12.01	−1.22	−0.40	−0.04
17	903.15	−12.01	−2.40	−0.40	−0.08
18	387.65	−6.42	−1.51	−0.50	−0.12
total				−2.69[b]	−0.48

[a] Frequencies in cm^{-1}, second derivatives in ppm a_0^{-2}, and shieldings in ppm. [b] The difference relative to the sum of the numbers above are due to a truncation of the reported contributions from the different vibrational modes, a truncation not used in the sum.

It would clearly be of interest to compare the relative chemical shifts of the various protons investigated in this study before and after zero-point vibrational corrections have been applied to the results, despite the fact that many of the zero-point vibrational corrections are fairly similar for several functionally different protons (e.g., alkyl and vinyl protons). For the hydrogens for which the differences are the largest compared to alkyl hydrogens, such as hydroxy- or amine-protons, it can be expected that there will be significant contributions to the experimentally observed proton shifts from hydrogen bonding in the liquid. Thus, to minimize the risk of hiding the effects of zero-point vibrational corrections in experimental solvent effects, we restrict ourselves to a comparison with experimental chemical shifts to the nonpolar molecules of this study.

Almost all experimental chemical shifts have been taken from the book of Brügel.[51] In this reference work, the chemical shifts of a large number of organic compounds in the liquid phase have been reported with respect to tetramethylsilane, as is common in NMR experiments. However, for easier comparison with our work, we report all chemical shifts relative to the nuclear shielding of methane. Both experimental and theoretical results are collected in Table 12. For the theoretical results, we report both the pure electronic contributions, the zero-point vibrationally corrected chemical shifts (using the relevant correction also for the reference to the methane molecule), and the results obtained using the electronic chemical shifts with our rule-of-thumb zero-point vibrational corrections added. We note from Table 12 that the calculated zero-point vibrational

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Table 12. Proton Shifts (in ppm) Relative to Methane for a Set of Non-Polar Molecules[a]

molecule	hydrogen atom	experiment	σ_e	$\langle\sigma\rangle_0$	$\langle\sigma\rangle$-(thumbrule)
methane	CH_3	0.00	0.00	0.00	0.00
ethane	CH_3	0.66	0.44	0.52	0.55
propane	CH_2	1.11	0.75	0.86	0.86
	CH_3	0.68	0.62/0.36	0.70/0.47	0.73/0.47
ethene	CH_2	5.07	5.16	4.77	5.03
propene	CH_2(*cis*)	4.64	4.60	4.52	4.47
	CH_2(*trans*)	4.73	4.79	4.74	4.66
	CH	5.49	5.65	5.60	5.52
	CH_3	1.48	1.23	1.29	1.34
cyclopropen	CH_2	0.69	0.47	0.59	0.57
	CH	6.82	7.02	7.03	6.89
ethyne	CH	1.58	0.98	1.15	1.15
propyne	CH	1.57	1.14	1.31	1.31
	CH_3	1.53	1.13	1.16	1.24
Butadiene	CH_2(trans)	4.83	4.93	4.76	4.80
	CH_2(cis)	4.93	4.76	4.64	4.63
	CH	6.04	6.11	6.06	5.98
1-butyne	CH	1.68	1.25	1.48	1.42
	CH_2	1.92	1.39	1.48	1.49
	CH_3	0.89	0.46/0.71	0.63/0.86	0.57/0.82
dimethyl ether	CH_3	2.98	2.89/2.24	2.89/2.28	3.00/2.35
oxirane	CH_2	2.31	1.68	1.71	1.79
benzene	CH	6.98	7.15	6.95	6.98
cyclopropane	CH_2	−0.03	−0.40	−0.28	−0.29
toluene	CH(ortho)	6.83	7.00	6.81	6.82
	CH(meta)	6.91	7.05	6.85	6.87
	CH(para)	6.82	6.90	6.76	6.72

[a] Equilibrium (σ_e) and vibrationally averaged ($\langle\sigma\rangle_0$) theoretical results are reported together with results obtained adding the thumb rule-corrections in Table 10 to the equilibrium values. For experimental data references, see text.

corrections for most of the nuclei brings the chemical shift relative to methane much closer to the experimentally observed shifts. This is perhaps most clearly illustrated for the chemical shifts of benzene and toluene, where the inclusion of the zero-point vibrational corrections brings the theoretical chemical shifts into spectacular agreement with experiment. The very small remaining differences (0.03 ppm for benzene and 0.02, 0.06, and 0.06 ppm for toluene) are expected to be of the order of residual errors in the theoretical calculations from an inadequate equilibrium geometry[35,32] as well as the neglect of solvent effects.

We have also tried to fit the theoretical results to experiment, both for the purely electronic estimates as well as for the zero-point vibrational corrected chemical shifts. For the electronic contributions to the chemical shifts, the linear regression leads to a fit

$$\delta_e = -0.44 + 1.09 \times \delta_{exp} \tag{4}$$

whereas a similar fit to the zero-point vibrationally corrected theoretical chemical shifts produces a fit that gives smaller differences between theory and experiment,

$$\delta_e^{zpv} = -0.28 + 1.04 \times \delta_{exp} \tag{5}$$

A few of the molecules deserve special attention, in particular the alkynes. It is unfortunate that neither ethene nor ethyne are tabulated in the book of Brügel but had to be taken from different sources,[52,53] making the direct comparison with experiment more difficult. However, ethyne appears to be an exception to the general rule that electron correlation effects do not alter hydrogen shieldings, as can be seen when comparing with recent high-level calculations by Wigglesworth et al.[29] Their best result for the hydrogen shielding is 30.24 ppm, to be compared with our SCF value 30.98 ppm. We also note that a similar correlation effect can be observed for the zero-point vibrational correction to the ethyne hydrogen shielding, the result of Wigglesworth et al. at the MCSCF level being −0.68 ppm,[29] as compared to our correction of −0.76 ppm. Using these correlated hydrogen shieldings gives us a chemical shift in ethyne relative to methane of 1.81 ppm, which is in much better agreement with experiment than our Hartree−Fock results. We assume, considering the differences compared to experiment for the chemical shifts of propyne and 1-butyne, that similar electron correlation effects may be present in these molecules. Although this may cause some concern for the validity of the corresponding zero-point vibrational corrections for these kinds of hydrogens, we note that the correlation effects are smaller for the vibrational corrections and probably contained in the uncertainty of these corrections as we report them in Table 10.

In Table 12 we have also listed the chemical shifts relative to methane when we apply our rule-of-thumb corrections in Table 10. To make the most relevant comparison, we have chosen to use the calculated zero-point vibrational correction to methane as it is, applying the rule-of-thumb corrections relative to the methane vibrational shift of −0.59 ppm. The results are indeed very encouraging. As seen from Table 10, the corrections follow the trend of the explicitly calculated values, and thus in almost all cases improve the agreement with experiment. Indeed, in certain instances, such as ethane and cyclopropene, the rule-of-thumb corrections are larger than the calculated corrections, providing even better agreement with experiment. Table 7 gives strong support for our rule-of-thumb zero-point vibrational corrections to hydrogen shielding constants and chemical shifts, and we recommend that they should always be added to theoretically calculated hydrogen shieldings obtained at the equilibrium geometry before a comparison is made with experiment.

V. Discussion and Summary

We have in the previous sections clearly demonstrated that, although zero-point vibrational corrections in general are considered to be small and negligible for all but the most accurate theoretical investigations, this cannot be considered to be the case for the zero-point vibrational corrections to hydrogen shielding constants and hydrogen chemical shifts. The zero-point corrections may be as large as −0.8 ppm for the proton shieldings, thus amounting to about 3−5% of the total shielding constant. However, considering that the total hydrogen shielding range is only about 10 ppm, the contribution from the zero-point vibrational motion may be as large as 10% of the total shielding scale, far exceeding the corrections due to electron correlation effects.[32] For an accurate theoretical estimate of the absolute hydrogen shieldings, zero-point vibrational effects *must* be taken into account.

We have demonstrated that—despite the fact that zero-point vibrational corrections to the hydrogen shieldings involve contributions from almost all normal modes in the molecule—the zero-point vibrational corrections to the hydrogen shieldings are transferable from one molecule to another for hydrogens belonging to the same kind of functional group. The corrections collected in Table 10 should provide a simple, yet accurate estimate of the corrections to electronic hydrogen shieldings caused by the molecular zero-point vibrational motion.

We have also demonstrated that even though the difference between the zero-point vibrational corrections to functionally

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different hydrogens are not as large as the full zero-point corrections themselves, they still lead to significantly improved agreement with experiment in the case of nonpolar molecules. We have observed that hydrogens in a polar group often display a very markedly different zero-point vibrational correction compared to aliphatic hydrogens (the difference between an alkyl proton and a hydroxy proton on average being 1.22 ppm). This observation will prove important for studies of hydrogen chemical shifts in the gas phase, whereas the effect will be hidden in comparison with the changes induced in the liquid phase because of hydrogen bonding to the protons in the hydroxy, carboxylic acid, or amine groups.

Although we have not explored the effects of electron correlation on the hydrogen shieldings and their zero-point vibrational corrections, there are indications that electron correlation effects do not contribute considerably to either of these contributions.[33,32] Thus, the results obtained for the zero-point vibrational corrections to the hydrogen shieldings may not be significantly altered by electron correlation effects, as also supported by the excellent agreement with experimentally observed chemical shifts we obtain after applying our zero-point vibrational corrections, as seen in Table 7. To the extent that differences remain, we believe the major cause is the determination of the equilibrium geometry, for which we have employed only Hartree−Fock wave functions.

We have also investigated the zero-point vibrational corrections to the other nuclei of the 38 molecules studied here. However, for these nuclei we expect electron correlation to be much more important, not only for the electronic contributions but also for the zero-point vibrational corrections, and thus our observations for these nuclei have to be considered less conclusive than for the hydrogen shieldings. Our results indicate that zero-point vibrational corrections to carbon, nitrogen, and in particular, oxygen may be significant. Furthermore, in contrast to our observations for the hydrogen shieldings, we find no sign of transferability of the zero-point vibrational corrections to the shieldings for these atoms, and it appears that calculations are needed for each individual molecule to assess the importance of zero-point vibrational corrections for these nuclear shieldings. However, the data collected in this paper may prove a useful starting point for estimating whether calculations of zero-point vibrational corrections are needed or not to be able to compare calculated chemical shifts with experiment. The zero-point vibrational corrections found for the oxygen shielding are very large, being almost 20 ppm in certain functional groups. Although this is a small effect compared to the electronic contribution to the shielding, oxygen shieldings appear to be an interesting target for more accurate studies of zero-point vibrational effects.[54]

Our investigation has also shed some light on the debate on whether an optimized MP2 structure or an experimental geometry should be used when calculating nuclear shieldings constants.[44,11] Although our approach for calculating the zero-point vibrational corrections may give some support for the use of a vibrationally averaged experimental geometry, thus recovering part of the vibrational effects, our results clearly demonstrate that the changes in the shielding arising from the shift of the expansion point is not necessarily the dominating contribution to the vibrational correction. More importantly, the two contributions to the zero-point vibrational corrections vary in relative importance from one shielding to another, and thus, one would risk including most of the ZPV corrections for one shielding but none (or even adding contributions going in the wrong direction of the overall corrections) for other shieldings, even if the overall total corrections were transferable. On this basis we would favor the use of theoretically optimized structures, as these geometries ensure that only electronic contributions are included when calculating the nuclear shielding constants for a given molecule.

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Supporting Information Available: Optimized and effective geometries in Cartesian coordinates and bohr, as well as all electronic and zero-point vibrational corrections to the isotropic shieldings of all 38 molecules investigated in this paper (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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