Role of zero-point vibrational corrections to carbon hyperfine coupling constants in organic radicals

X. Chen, Z. Rinkevicius, K. Ruud, and H. Ågren

Role of zero-point vibrational corrections to carbon hyperfine coupling constants in organic π radicals

X. Chen,[1] Z. Rinkevicius,[1,2,a)] K. Ruud,[3] and H. Ågren[1]

[1]*KTH Royal Institute of Technology, School of Biotechnology, Division of Theoretical Chemistry and Biology, S-106 91 Stockholm, Sweden*
[2]*KTH Royal Institute of Technology, Swedish e-Science Research Center (SeRC), S-100 44, Stockholm, Sweden*
[3]*Centre for Theoretical and Computational Chemistry, Department of Chemistry, University of Tromsø, N-9037 Tromsø, Norway*

By analyzing a set of organic π radicals, we demonstrate that zero-point vibrational corrections give significant contributions to carbon hyperfine coupling constants, in one case even inducing a sign reversal for the coupling constant. We discuss the implications of these findings for the computational analysis of electron paramagnetic spectra based on hyperfine coupling constants evaluated at the equilibrium geometry of radicals. In particular, we note that a dynamical description that involves the nuclear motion is in many cases necessary in order to achieve a semi-quantitatively predictive theory for carbon hyperfine coupling constants. In addition, we discuss the implications of the strong dependence of the carbon hyperfine coupling constants on the zero-point vibrational corrections for the selection of exchange-correlation functionals in density functional theory studies of these constants. © *2013 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4789769]

I. INTRODUCTION

Despite the fact that electron paramagnetic resonance (EPR) spectroscopy for a long time has been instrumental in analyzing spin density distributions in organic π radicals,[1–6] it is not until quite recently that first principles theories have been developed, having an accuracy that allow them to be useful for interpreting experimental spectra of such radicals.[7–18] The lack of such analysis tools forced early investigations of EPR data to rely on rules-of-thumb or simple principles that relate the spin density to the measured hyperfine coupling constants (HFCCs). One such relation is the McConnell relation that states that the spin density ρ_C on the carbon of a C–H fragment in an organic π radical is linearly dependent on the isotropic hyperfine constant of hydrogen.[1–3] Although such relations or structure-property tools have frequently been used in the field of EPR,[4–6] recent advances in the quantum chemical modeling of HFCCs in organic radicals[7–18] offer an alternative way for exploring the physical origin of these constants.

Historically, vibrational effects on HFCCs have been assumed to be insignificant except for special cases such as the methyl radical,[11,12,19–24] and most investigations of HFCCs have, therefore, been carried out by simply ignoring vibrational effects.[8–10,13,15–18] The vibrational contributions to hyperfine coupling constants can be separated into zero-point and temperature-dependent vibrational corrections. These refer to the vibrational part of the total wave function at zero temperature and, respectively, the ensemble of molecular excited vibrational states occupied at the temperature of measurement, as well as corrections due to centrifugal distortions.[25,26] Unfortunately, both parts are hard to extract

experimentally except for a few stable radicals.[27–29] This has restricted the development of empirical guidelines for identifying the occurrence of significant vibrational corrections. Recent developments in computational technology, in particular, open-shell density functional theory,[12,14,30] now allows for systematic studies of vibrational corrections to HFCCs for general organic radicals as well as paramagnetic transition metal complexes and can thereby advance our understanding of the role of vibrational corrections. Our recent work[30] indicates that the importance of zero-point vibrational corrections (ZPVCs) to hyperfine coupling constants is not limited to radicals which have flexible structures, such as the methyl radical, but that they indeed also are important for other types of radicals and thus need to be critically assessed. It is the purpose of this study to examine the importance of ZPVCs to carbon hyperfine coupling constants in organic π radicals. In Sec. II, we give a short outline of the methodology used for evaluating ZPVCs to isotropic HFCCs and briefly describe other computational details; in Secs. III and IV, we present our results and give some concluding remarks and an outlook.

II. THEORY AND COMPUTATIONAL DETAILS

The perturbation theory approach for evaluation of vibrational corrections,[25,26] which is based on the vibrational wavefunction expansion around an effective geometry,[31] has been successfully applied to study vibrational effects on various optical and magnetic properties.[30,32–34] In our previous study of hydrogen HFCCs in allylic radicals,[30] we employed this approach to compute ZPVCs to HFCCs of medium-sized radicals. Following this success, we adopt in this work the same computational strategy for evaluation of ZPVCs to carbon HFCCs in organic π radicals. For sake of completeness,

a)Electronic mail: rinkevic@theochem.kth.se.

we here briefly recapitulate the main steps of the computational procedure used to determine ZPVCs to HFCCs. Following our previous work,[30] this procedure consists of three steps. First, the effective geometry of the molecule $\{R_{\text{eff}, K}\}$ must be determined from[31]

$$\{R_{\text{eff}, K}\} = \{R_{eql, K}\} - \frac{1}{4\omega_K^2} \sum_L \frac{V_{eql, KLL}^{(3)}}{\omega_L}, \quad (1)$$

where the equilibrium geometry $\{R_{eql, K}\}$ is obtained via a conventional geometry optimization procedure, and the vibrational frequencies $\{\omega_K\}$ along with cubic force field constants $\{V_{eql, KLL}^{(3)}\}$ at the equilibrium geometry are computed using numerical differentiation following the guidelines described in Ref. 30. In the second step, derivatives of the direct spin density and spin polarization contributions to the isotropic HFCC of the nth atom, $\partial^2 A_{n,\text{eff}}^{\text{den,iso}} / \partial Q_K^2$ and $\partial^2 A_{n,\text{eff}}^{\text{pol,iso}} / \partial Q_K^2$, are determined along the normal modes at the effective molecular geometry via numerical differentiation of the HFCCs computed using the density functional restricted-unrestricted (DFT-RU) approach.[35–37] For an exact definition of the direct spin density and spin polarization contributions to the HFCC in the DFT-RU approach, we refer the reader to the original works on the approach.[35–37] In the third step, the isotropic HFCC of the nth atom, $A_{n,eql}^{\text{iso}} = A_{n,eql}^{\text{iso,den}} + A_{n,eql}^{\text{iso,pol}}$, is computed at the equilibrium geometry, and the harmonic and anharmonic ZPVCs to $A_{n,eql}^{\text{iso}}$ determined according to the expressions

$$A_{n,\text{vib}}^{\text{iso,har}} = \frac{1}{4} \sum_K \frac{1}{\omega_K} \frac{\partial^2 A_{n,\text{eff}}^{\text{iso}}}{\partial Q_K^2}, \quad (2)$$

$$A_{n,\text{vib}}^{\text{iso,anh}} = A_{n,\text{eff}}^{\text{iso}} - A_{n,\text{eql}}^{\text{iso}}, \quad (3)$$

respectively. Similar to the case of the equilibrium geometry, we here write the isotropic HFCC at the effective geometry as the sum of direct spin density and spin polarization contributions, i.e., $A_{n,\text{eff}}^{\text{iso}} = A_{n,\text{eff}}^{\text{iso,den}} + A_{n,\text{eff}}^{\text{iso,pol}}$. Taking this into account, the total ZPVCs to the isotropic HFCCs of the nth atom can be written as the sum of the above given ZPVCs, i.e., $A_n^{\text{iso,zvpc}} = A_{n,\text{vib}}^{\text{iso,har}} + A_{n,\text{vib}}^{\text{iso,anh}}$. Thus, an isotropic HFCC of the nth atom in an investigated radical at 0 K is rigorously defined as the sum of its value at the equilibrium geometry and its ZPVC, i.e., $A_n^{\text{iso}} = A_{n,\text{eql}}^{\text{iso}} + A_n^{\text{iso,zpvc}}$.

We employ the same set of computational parameters in this study of carbon HFCCs in organic π radicals as in our previous work devoted to hydrogen HFCCs in allylic radicals.[30] This choice is motivated by two factors, namely, the well-established performance of the selected combination of basis sets and exchange-correlation functionals in the description of the force field and HFCCs of radicals, and the relatively low cost of these calculations, making investigations of medium-sized radicals possible. Thus, following our previous work,[30] the equilibrium and effective geometries as well as force fields at these geometries have been determined using the B3LYP exchange-correlation functional[38–41] and the TZV2P basis set,[42] and computations of the isotropic HFCCs and their second derivatives with respect to normal modes have been done using the DFT-RU approach[35–37] (numerical

TABLE I. Isotropic HFCC of carbon atom (^3P) computed with various methods.

Method	Basis set	A_{iso}, G[a]	Ref.
MCSCF	Numnerical	8.78	64
MR-CISD	23s12p10d4f2g	6.35	64
CCSD(T)	23s12p10d4f2g	7.64	47
DFT-RU	Huz-IIIsu3	8.81	This work

[a]Isotropic hyperfine coupling constant of carbon atom computed at the equilibrium geometry.

differentiation step size has been set to 0.0075 a.u.). In the carbon HFCCs calculations, we also employed the B3LYP exchange-correlation functional,[38–41] which is typically recommended for computation of HFCCs of radicals,[15,17] and the Huz-IIIsu3 basis set,[43–46] which is tailored for evaluation of HFCCs. To validate our choice of exchange–correlation functional and basis set for carbon HFCCs, we tested the performance of our methodology on a single carbon atom in its ^3P ground state. The results of this test are presented in Table I, and indicate that the DFT-RU method overestimates the isotropic HFCC value by roughly 1.2 G compared to the most accurate CCSD(T) results.[47] Overall, the DFT-RU method predicts the carbon atom isotropic HFCC with an accuracy comparable to numerical MCSCF (see Table I). Considering the reasonable results obtained for the carbon atom HFCC, we have used the DFT-RU method for computations of vibrationally corrected carbon isotropic HFFFCs in medium-sized organic π radicals, as the DFT-RU method is an affordable compromise between accuracy and computational cost.

All calculations have been carried out using a development version of the DALTON 2011 quantum chemistry package.[48]

III. RESULTS AND DISCUSSION

In this work, we study carbon HFCCs for a set of organic π radicals (see Fig. 1), which includes methyl, benzyl, p-benzoquinone, fulvalene, and the tropone anion radicals. The main selection criterion for these radicals has been the requirement that at the equilibrium geometry,
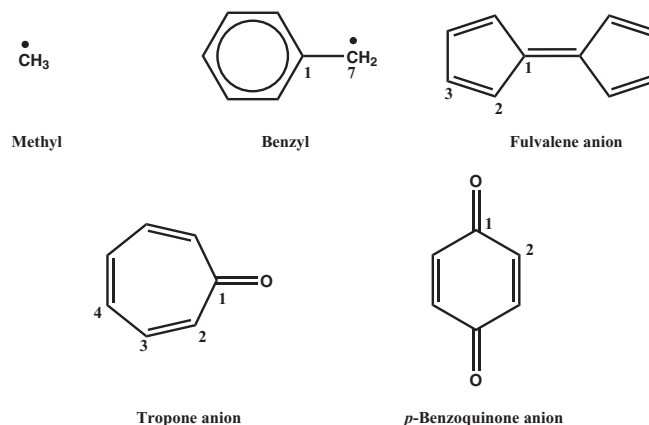

FIG. 1. Selected set of organic π radicals for which isotropic carbon HFCCs has been investigated in this work.

TABLE II. Carbon isotropic HFCC in methyl radical $CH_3(^2A'')$.

Method/Basis set	A_{eql}^{iso}, G[a]	A_{vib}^{iso}, G[b]	ΔA_{vib}^{iso}, G[c]	Temp. (K)	Ref.
B3LYP[d]/Huz-IIIsu3	29.9	42.2	12.3 (41%)	0	This work
P(CI)/DZ	22.2	35.1	12.9 (58%)	96	20
QCISD(T)/TZVP$^-$	27.8	37.7	9.9 (36%)	96	21
MCSCF/cc-pVTZus2st	27.7	37.3	9.6 (35%)	0	23
UB3LYP/EPR-III	28.2	28.7	0.5 (2%)	100	24
CISD/DZ	25.7	…	…	…	49
CCSD(T)/Chipman	28.5	…	…	…	11
B3LYP[d]/Huz-IVu4s	30.1	…	…	…	35
UB3LYP/EPR-III	28.6	…	….	…	15
UB3LYP/N07D	28.7	…	….	…	17
UB2PLYP/EPR-III	30.0	…	…	…	18
OO-RI-MP2/EPR-III	25.5	…	…	…	18
OO-SCS-RI-MP2/EPR-III	22.0	…	…	…	18
CCSD(T)/EPR-III	24.7	…	…	…	18
Experiment[e]	27.0	38.3	….	96	61

[a]Isotropic hyperfine coupling constant of carbon computed at the equilibrium geometry.
[b]Isotropic hyperfine coupling constant of carbon with added zero-point vibrational corrections.
[c]Zero-point vibrational corrections and in parentheses their relative size with respect to A_{eql}^{iso} in percents.
[d]Isotropic HFCC values computed using restricted-unrestricted method.
[e]Absolute values of experimentally measured isotropic hyperfine coupling constants of carbon.

the carbon isotropic HFCCs of interest are solely defined (in a static picture) by spin polarization. This selection criterion increases the probability that ZPVCs will play a significant role in defining the total value of the isotropic HFCCs, as the direct spin density contribution to the HFCCs only becomes accessible via vibrational corrections. The methyl and benzyl radicals have been extensively studied previously[11, 12, 19, 20, 22–24, 49–52] and the importance of vibrational corrections to HFCCs in these radicals are by now well established. Among the anion radicals, only p-benzoquinone has been extensively investigated in the past,[53–59] as it represents the simplest possible model of a quinone-type electron acceptor in bacterial and plant photosystems.[12, 53, 54] However, to the best of our knowledge, vibrational effects on carbon HFCCs have so far have not been studied for any of the here selected anion radicals.

A. Methyl radical ($^2A''$, D_{3h} symmetry)

The methyl radical is a prototypical π radical with an unpaired electron residing in an a'' orbital which consists almost entirely of the $2p_z$ orbital of the carbon atom. Due to its importance for various chemical processes, the electronic structure, hydrogen and carbon HFCCs of this radical have been extensively investigated.[11, 12, 15, 17–24, 35, 49–52] According to previous works,[11, 20, 23] the accurate determination of carbon HFCC requires a balanced description of spin polarization and simultaneous account of vibrational effects. These features make this system a critical test case not only for the DFT-RU approach[35–37] itself, but also for the ZPVCs to the HFCCs computational procedure outlined in Sec. II. To evaluate the accuracy of our computational strategy, we tabulate in Table I the carbon isotropic HFCC in the methyl radical as computed in this work and in several representative previous studies.[11, 15, 17, 18, 20, 21, 23, 24, 35] As one can see from Table I, our DFT-RU calculations give the correct physical picture of the

carbon isotropic HFCC and show that its value is strongly dependent on vibrational corrections, which constitute around 41% of the total HFCC value at 0 K. However, quantitative agreement between our results and experimental data is not achieved as the computed HFCC overestimates the experimentally measured data by 3.9 G (see Table II). There are several possible sources for these discrepancies, of which we believe limitations in the B3LYP functional in describing spin polarization effects is the only likely source of these errors.

Our results obtained with the B3LYP/Huz-IIIsu3 are in very good agreement with our previous results obtained using B3LYP/Huz-IVu4s,[35] suggesting that basis truncation errors are small. In a similar manner, environments effects are also expected to be small,[61] as the experimental data have been collected in liquid methane which is considered to be a nonpolar, weakly interacting solvent. This conclusion is further supported by a study of Fernandez *et al.*[23] that showed that the solvent shift on the carbon HFCC in the methyl radical in methane is about -0.37 G relative to the vacuum, calculated for a rigid methyl radical.

Temperature effects can also be expected to be small, because the EPR measurements have been carried out at 96 K.[61] Ellinger *et al.*[20] have shown that temperate-dependent vibrational corrections will only gain magnitude for temperatures above 200 K, where the temperature effects are about 0.3 G for the carbon HFCC in the methyl radical. We note, however, that an *ab initio* molecular dynamics simulation by Tachikawa *et. al.*[24] reached a somewhat different conclusions, in which temperature were significant already at 100 K and larger at 200 K, about 0.5 G. However, as their study fail to reproduce the experimentally observed carbon HFCC in the methyl radical (see Table II) and because of the lack of a quantum description of the nuclear motion, we consider this result less reliable and conclude in agreement with Ellinger *et al.*[20] that temperature effects should be small at the temperatures used in the experiments with which we compare out results.

TABLE III. Carbon isotropic HFCC in benzyl radical $C_6H_5CH_2(^2B_1)$.

Method/Basis set	Atom	A_{eql}^{iso}, G[a]	A_{vib}^{iso}, G[b]	ΔA_{vib}^{iso}, G[c]	Temp. (K)	Ref.
B3LYP[d]/Huz-IIIsu3	C_1	−14.2	−14.2	≈0.0 (≈0%)	0	This work
	C_7	21.5	27.4	5.9 (27%)	0	This work
UB3LYP/EPR-II	C_7	21.8	25.6	3.8 (17%)	RT	52
UB3LYP/EPR-III	C_1	−13.7	…	….	…	15
	C_7	20.4	…	….	…	15
UB3LYP/N07D	C_1	−13.6	…	….	…	17
	C_7	21.0	…	….	…	17
Experiment[e]	C_1	…	14.5	….	RT	62
	C_7	…	24.5	….	RT	62

[a]Isotropic hyperfine coupling constant of carbon computed at the equilibrium geometry.
[b]Isotropic hyperfine coupling constant of carbon with added zero-point vibrational corrections.
[c]Zero-point vibrational corrections and in parentheses their relative size with respect to A_{eql}^{iso} in percents.
[d]Isotropic HFCC values computed using restricted-unrestricted method.
[e]Absolute values of experimentally measured isotropic hyperfine coupling constants of carbon.

Thus, the only source for the large discrepancy between our computed and experimental carbon HFCCs is the overestimation of the spin polarization effect by the B3LYP exchange–correlation functional. We have previously observed that the B3LYP functional overestimates spin polarization in a few organic radicals, including the methyl radical.[35] Recent work by Hermosilla *et. al.*[15] and Barone *et al.*,[17] based on the conventional unrestricted DFT formalism, overestimation of the carbon HFCC in the methyl radical has also been observed (see Table II). Taking these findings into account, we conclude that most probably the reason for the large of discrepancy 3.9 G between our computed carbon HFCC and experimental data is caused by an overestimation of spin polarization by the B3LYP functional. Comparing our DFT-RU results with QCISD(T)/TZVP- results (see Table II), we see that compared to the accurate QCISD(T)/TZVP reference data, this discrepancy arises to an equal extent from an overestimation the carbon HFCC at the equilibrium geometry (2.1 G) and of the vibrational correction to the carbon HFCC (2.4 G).

Our results show that vibrational corrections are extremely important in this system and amounts to 41% of the total value of the carbon HFCC (see Table II), in agreement with earlier work.[20, 21, 23] From the analysis above and based on the results in Table II, we conclude that the most important factor defining the accuracy of our calculations is the ZPVCs to the HFCC, as these corrections are much larger than the contributions given by environmental effects, basis set truncation errors, and errors in the exchange-correlation functional. The methyl radical very eloquently illustrates the importance of vibrational effects in computations of hyperfine coupling constants, where the vibrational corrections play a critical role not only for obtaining quantitative, but also qualitative, agreement with experimental observations.

B. Benzyl radical ($^2B_1$, C_{2v} symmetry)

The benzyl radical has a similar electronic structure as the methyl radical, with a single unpaired electron residing in a b_1 orbital predominantly localized on the carbon atom of the $-CH_2$ fragment (position seven in the benzyl radical, see

Fig. 1). The carbon isotropic HFCCs have been measured for the carbon atom in the $-CH_2$ group and the ring carbon atom C_1 (position 1 in the benzyl radical, see Fig. 1), which is the benzene ring connection point with the $-CH_2$ group. In an earlier work, Adamo *et. al.*[52] concluded that of these two carbon atoms, only the HFCC of the first one shows a strong dependence on vibrational corrections (see Table III), and that these corrections constitute around 17% of the total HFCC value. Our DFT-RU calculations reproduce these findings, i.e., we find that the ZPVC to the HFCC of C_7 is around 27%, or 5.9 G, and that the ZPVC to the HFCC of C_1 is negligible and does not exceed 0.04 G. Thus, it is clear that for the carbon atom C_1, which is rigidly locked in the benzene ring and have no freedom for large-amplitude motion, the conventional way of computing HFCC without considering vibrational corrections is appropriate. This conclusion is also expected to hold for the remaining carbon atoms in the benzene ring for which the HFCCs have not yet been determined experimentally.

Let us turn now to the carbon at position seven in the benzyl radical (see Fig. 1), which in all respects (bonding pattern, localization of unpaired electron, etc.) is very similar to the carbon atom in the methyl radical. As we already discussed, the HFCC of this carbon is significantly influenced by vibrational corrections, and the ZPVC to the HFCC is 5.9 G according to our B3LYP/Huz-IIIsu3 results (see Table III). In this particular case, the carbon HFCC obtained with the DFT-RU method at the equilibrium geometry underestimates the EPR measurement at room temperature by 3 G (see Table III), while the HFCC value corrected with ZPVCs overestimates these experimental results by 2.9 G. Similar to the methyl radical case, the reasons for this discrepancy can be traced to the neglect of environmental effects, neglect of the temperature-dependent part of the vibrational corrections and deficiencies in the B3LYP functional in describing the spin polarization effects. However, in this case, and in contrast to the methyl radical, we expect a more pronounced contribution from the temperature-dependent vibrational corrections at the temperature of the EPR measurement because of the higher temperature used in experiment. Taking into account the similarity of the carbon C_7 atom in the benzyl and methyl

radicals, we can estimate that the temperature-dependent vibrational corrections to this carbon HFCC is in the range 1–2 G (assuming a similar temperature dependence of the carbon C_7 as the one obtained by Ellinger *et. al.*[20] for the methyl radical). Thus, the inclusion of the temperature-dependent part of the vibrational correction will overall worsen the agreement between the computed and experimentally measured carbon C_7 HFCCs. This negative effect of the temperature-dependent vibrational corrections on the overall agreement with experiment will be partially compensated if one considers the environmental effects, which will give a negative solvent shift for the carbon C_7 HFCC in the benzyl radical. However, the solvent shift from the adamantane matrix used in the EPR experiment[62] will at the most be -1.5 G judging from the typical solvent shifts of HFCCs induced by nonpolar solvents.[12] We conclude that due to the opposite sign of these two approximations in our calculations, they partially cancel each other and thus cannot be responsible for the major part of the 2.9 G discrepancy between our DFT-RU and experimental results for the carbon C_7 HFCC. Therefore, similar to the methyl radical case, we can attribute the overestimation of the experimental results for carbon C_7 HFCC to the shortcomings of the B3LYP exchange-correlation functional in describing spin polarization in the benzyl radical. We emphasize that the DFT-RU approach gives carbon HFCC values in the benzyl radical very close to the ones obtained by the conventional unrestricted DFT by Hermosilla *et al.*[15] and Barone *et al.*[17] (see Table III) and consequently the different ways of accounting for spin polarization lead to essentially the same results, indicating that the exchange-correlation functional used is the source of the observed discrepancies.

According to the above given analysis of our DFT-RU results, the carbon HFCCs in the benzyl radical show a different behavior with respect to vibrational corrections: The HFCCs of the carbon atom located in the benzene ring are not influenced by vibrational effects to any significant extent, while the HFCC of the carbon in the $-CH_2$ group is strongly affected by vibrational corrections. Here, ZPVCs amount up to 5.9 G and temperature-dependent vibrational corrections amount to 1–2 G (estimate based on the results of Ellinger *et al.*[20] for the methyl radical). From all additional physical mechanisms contributing to the carbon HFCC value beyond the static evaluation of this constant in vacuum at the equilibrium geometry, the zero-point vibrational corrections give the biggest contribution for the C_7 carbon, being at least twice as large as other contributions arising from the temperature-dependent vibrational contributions to the HFCC or the environmental contribution. Thus, in the case of the benzyl radical, the isotropic HFCC of the carbon atom in the $-CH_2$ group can be evaluated reliably only when ZPVCs are included in the computations.

C. p-Benzoquinone anion radical ($^2B_{2g}$, D_{2h} symmetry)

Among the anion radicals studied in this work, the p-benzoquinone anion radical has been the most extensively investigated by experimental and theoretical methods,[53–60] as it serves as the simplest model for quinone-type electron ac-

TABLE IV. Carbon isotropic HFCC in p-benzoquinone anion radical $C_6H_4O_2^-$ ($^2B_{2g}$).

Method/Basis set	Atom	A_{eql}^{iso}, G[a]	A_{vib}^{iso}, G[b]	ΔA_{vib}^{iso}, G[c]	Ref.
B3LYP[d]/Huz-IIIsu3	C_1	-3.2	-2.7	0.5 (16%)	This work
	C_2	-0.2	0.3	0.5 (250%)	This work
UB3LYP/D95(d,p)	C_1	-3.7	….	….	59
	C_2	-0.2	….	….	
UPW86/6-311G($2d,p$)	C_1	-3.7	….	….	58
	C_2	-0.1	….	….	
Experiment[e]	C_1	…	2.1…-0.2	….	53
	C_2	…	0.1–0.7	….	58

[a]Isotropic hyperfine coupling constant of carbon computed at the equilibrium geometry.
[b]Isotropic hyperfine coupling constant of carbon with added zero-point vibrational corrections.
[c]Zero-point vibrational corrections and in parentheses their relative size with respect to A_{eql}^{iso} in percents.
[d]Isotropic HFCC values computed using restricted-unrestricted method.
[e]Experimentally measured isotropic hyperfine coupling constants of carbon.

ceptors in various biological systems, including bacterial and plant photosystems. In this system, the unpaired electron resides in a b_{2g} π-type orbital primarily localized on the oxygen atoms of the carboxyl groups, and due to this particular structure of the singly-occupied orbital, only carbons in the carboxyl group (see position one in Fig. 1) show non-negligible spin density population. These features of p-benzoquinone lead to overall small carbon HFCCs, where the isotropic HFCCs for the carbon C_1 atom in the carboxyl groups are around -3.7 G according to results of various previous calculations (see Table IV) and the isotropic HFCCs for the remaining four carbon atoms (position two in Fig. 1) are close to zero. Our calculations overall reproduce these previous results, predicting the HFCC of C_1 to be -3.2 G and of C_2 to be -0.2 G at the equilibrium geometry. Before examining the ZPVCs to the HFCCs it is instructive to look at the resonant valence bond structures of the p-benzoquinone anion radical, which are given in Fig. 2. As seen from Fig. 2, p-benzoquinone anion radical lack symmetric resonant valence bonds structures, and thus one can expect significant ZPVCs to carbon HFCCs due to strong localization of the spin density and spin polarization contributions that are responsible for the magnitude of the carbon HFCCs. The ZPVCs for both types of carbon atoms are around 0.5 G (in terms of absolute values), but adding these corrections to the HFCCs have different qualitative effects on the different carbon atoms. In the case of the carbon atoms in the carboxyl groups (see C_1 in
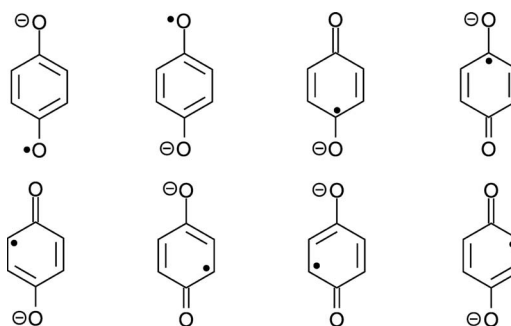

FIG. 2. Resonant valence bond structures of p-benzoquinone anion radical.

Table IV), inclusion of ZPVCs for the HFCC only adjust the magnitude of the HFCC, decreasing it by 16% (in terms of absolute values) from -3.2 G to -2.7 G. The effect of adding ZPVCs to the equilibrium geometry HFCC is much more pronounced for the second type of carbon atoms in the p-benzoquinone anion radical (see C_2 in Table IV), where the ZPVCs are around 2.5 times larger than the HFCC itself at the equilibrium geometry. The addition of ZPVCs changes not only the total magnitude, but also the physical interpretation of the HFCC constant due to the change of the sign of the HFCC from negative to positive. To the best of our knowledge, this is the first time where a change of carbon HFCC sign due to vibrational corrections have been predicted. However, here we would like to emphasize that this effects is observed for very small values of carbon HFCCs and more accurate calculations, which go beyond DFT methods, are needed to verify this finding. This example clearly shows that even determining the sign of small HFCCs based on static calculations without considering nuclear motion can be dangerous and lead to qualitatively wrong conclusions. Therefore, we would suggest to exercise caution when assigning signs of HFCC constants with small absolute values from static *ab initio* or DFT calculations, as the vibrational effects, and in particular the ZPVCs, can change the sign of the HFCCs and consequently alter the interpretation of the electron spin density distribution.

After discussing the importance of ZPVCs for the carbon HFCCs in the p-benzoquinone anion radical in vacuum, let us turn to the real experimental situation in which EPR measurements are performed in solution. The first question to answer is how important the vibrational corrections are compared to environmental effects? The answer to this question is nontrivial since the carbon HFCCs in the p-benzoquinone anion radical show a strong dependence on the type of environment. For example, the carbon HFCCs in the carboxyl groups change from 2.1 G to -0.2 G going from dimethyl sulfoxide (DMSO) to water according to available experimental data.[53] Our DFT-RU results for this type of carbon atoms overestimate (in absolute value) the experimentally measured HFCCs in DMSO solution by 0.6 G (see Table IV). Here, in contrast to the previously discussed methyl and benzyl radicals, we cannot rule out the importance of environmental effects and that these effects, combined with the tendency of the B3LYP functional to overestimate spin polarization effects, can be responsible for the discrepancy between the computed and experimental values of the HFCC for the C_1-type carbon atoms in the p-benzoquinone anion radical.

The situation with the other type of carbon atom, namely, C_2 (see Fig. 1), is very similar; its HFCC show significant solvent dependence and change from 0.1 G to 0.7 G (see Table IV). Here, again due to the overall small magnitude of the HFCC itself, the role of the ZPVC is expected to be more prominent and of similar importance as for the p-benzoquinone anion radical in vacuum.

Summarizing the discussion of carbon HFCCs in the p-benzoquinone anion radical, we conclude that due to the overall small size of these HFCCs, they are significantly influenced by ZPVC corrections, and these corrections must be accounted for together with environmental effects due to the

TABLE V. Isotropic HFCCs of carbon in fulvalene ($^2B_{3g}$) and tropone ($^2A_2$) anion radicals determined using DFT-RU method.

Radical	Atom	A_{eql}^{iso}, G[a]	A_{vib}^{iso}, G[b]	ΔA_{vib}^{iso}, G[c]	A_{exp}^{iso}, G[d]	Ref.
Fulvalene	C_1	2.07	2.80	0.73 (35%)	2.90	65
anion	C_2	-1.19	-0.64	0.55 (46%)	1.40	
	C_3	1.44	2.39	0.95 (66%)	2.15	
Tropone	C_1	-8.32	-7.76	0.56 (7%)	8.32	66
anion	C_2	10.91	12.77	1.86 (17%)	12.33	
	C_3	-6.60	-5.87	0.73 (11%)	6.02	
	C_4	-3.92	-5.33	1.41 (36%)	4.54	

[a]Isotropic hyperfine coupling constant of carbon computed at the equilibrium geometry.
[b]Isotropic hyperfine coupling constant of carbon with added zero-point vibrational corrections.
[c]Zero-point vibrational corrections and in parentheses their relative size with respect to A_{eql}^{iso} in percents.
[d]Experimentally measured isotropic hyperfine coupling constants of carbon.

strong dependence of these HFCCs on the local solvent environment and hydrogen bonding effects.

D. Fulvalene anion radical ($^2B_{3g}$, D_{2h} symmetry)

The fulvalene anion radical has attracted less attention than the previously discussed π radicals, and to the best of our knowledge no computational investigation has been carried out for the carbon HFCCs of this radical. The size of the carbon HFCCs of the fulvalene anion radical are rather similar to the previously discussed p-benzoquinone anion; the experimentally measured HFCCs are 1–3 G (see Table V). However, the electronic structure of fulvalene is quite different from that of the p-benzoquinone anion radical, with the unpaired electron residing in the b_{3g} orbital consisting of $2p_z$ atomic orbitals of carbon atoms in the former case. In agreement with our expectations, the ZPVCs to the carbon HFCCs in this anion radical contribute significantly to the total magnitude of the HFCCs; these contributions are around 35%–66% of the HFCC computed at the equilibrium geometry. Thus, inclusion of ZPVCs is crucial in computations of carbon HFCCs of the fulvalene anion radical. We note, however, that in terms of absolute values, the ZPVCs do not exceed 1 G and thus becomes significant only due to the small size of the carbon HFCCs at the equilibrium geometry. Comparing our DFT-RU results with experimental data, we see that the addition of ZPVCs improves agreement (see Table V) and decreases the mean absolute deviation from 0.7 G to 0.4 G. As before, the remaining discrepancies between our results and experimental data can be attributed to the neglect of environmental effects and the choice of exchange-correlation functional.

E. Tropone anion radical ($^2A_2$, C_{2v} symmetry)

The tropone anion radical is the largest π-type radical investigated in this work. It consists of 14 atoms and has one unpaired electron localized in an a_2 orbital which can largely be described as a carbon $2p_z$ atomic orbital without any contribution from the oxygen atomic orbitals. This feature of the electronic structure ensures that the spin density is distributed over the entire seven-membered ring (see Fig. 1), and consequently the experimentally measured carbon HFCCs

constants in this radical are between 4.5 G and 12.3 G (see Table V). Therefore, by the magnitude of the carbon HFCCs, this radical anion is in between the methyl-like π radicals with large carbon HFCCs and the benzoquinone anion-like π radicals with small carbon HFCCs. According to the results presented in Table V, the ZPVCs play a moderate role in this radical, contributing to the total HFCC by 7%–36% of the carbon HFCC at the equilibrium geometry (see Table V). In terms of the absolute values, the ZPVCs do not exceed 2 G and are thus probably of comparable size to environment effects and errors introduced by the choice of exchange-correlation functional. Thus, as for the other anion radicals studied in this work, the overall importance of the ZPVCs to carbon HFCCs is comparable to other factors that affect the accuracy of our calculations, such as environment effects, and these effects must be accounted for on an equal footing in order to obtain reliable predictions of carbon HFCCs in π radicals of the kind studied here.

IV. DISCUSSION AND CONCLUDING REMARKS

Carbon isotropic HFCCs of all organic radical investigated in this work are defined solely by spin-polarization effects at the equilibrium geometry (in the static picture). Despite the common physical origin of these constants, the size of the ZPVCs to these constants vary widely going from one carbon atom to another. Furthermore, the importance of zero-point vibrational contributions from different vibrational modes change drastically going from one radical to another: for methyl and benzyl radical (C_7 carbon), ZPVCs to carbon isotropic HFCCs are dominated by the contribution of a single vibrational mode corresponding to the umbrella motion, whereas for the remaining radicals at least several vibrational modes (up to 7) contribute significantly to the ZPVCs. Thus, the overall importance of ZPVCs to HFCC is highly specific to each carbon atom and depends on its local structural environment as well as the distribution of spin density in the radical. However, in our calculations of the carbon HFCCs in organic π radicals we observed three trends in the behavior of the ZPVCs to the carbon HFCCs: (1) for carbon atoms for which the π orbital containing the unpaired electron is localized, the ZPVCs to their HFCCs are typically large (up to 50% of the total HFCC magnitude) and thus the inclusion of ZPVCs is essential in order to obtain a physically correct and (semi)quantitative agreement between theoretical calculations and experimental data; (2) for carbon atoms with medium-sized HFCCs (absolute values between 5–15 G), the ZPVCs to their HFCCs in most cases do not exceed 1–2 G and are thus of similar importance as the environmental effects in the calculation of HFCC; (3) for carbon atoms with small HFCCs (absolute values up to 5 G), the ZPVCs to their HFCCs are typically relatively large and in extreme cases exceed the HFCCs values at the equilibrium geometry. We expect these trends to be applicable beyond the limited set of organic radicals investigated in this work, and we hope these trends will provide guidelines for judging whether to consider ZPVCs in practical calculations of carbon HFCCs or not.

This work suggests that ZPVCs to isotropic HFCCs are more pronounced for carbon atoms than for hydrogen atoms in organic radicals. In this work, we observed that ZPVCs to carbon isotropic HFCCs are around 0.5–2 G, and in special cases such as the benzyl or methyl radicals can become even larger, 5.9 G and 12.3 G, respectively. In the case of ZPVCs to hydrogen isotropic HFCCs, which have been studied in our previous work,[30] the magnitude of these corrections never exceeded 1.5 G and were in many cases less than 0.3 G. Thus, the ZPVCs to hydrogen and carbon HFCCs behaves differently and in many cases, even in the same molecular system, the ZPVCs corrections can be neglected for hydrogen HFCCs but not for the carbon HFCCs.

This work highlights the importance of zero-point vibrational corrections to carbon hyperfine coupling constants in organic π radicals. In particular, our investigation has demonstrated that the coupling between electronic and vibrational degrees of freedom in radicals in many cases are important, and more reliable (semi-)quantitative description of carbon HFCCs require not only an accurate description of the spin density and spin polarization, but also an account of zero-point vibrational effects. Furthermore, in the extreme case of the ring carbons of the p-benzoquinone anion radical, the inclusion of zero-point vibrational corrections in our DFT-RU calculations induces a sign change of the hyperfine coupling constants, and this is the first system in which such a behavior has been observed. This finding should be kept in mind when analyzing spin density distributions in organic radicals based on electron paramagnetic resonance data and conventional HFCC calculations (carried out at the equilibrium geometry without taking into account ZPVCs) as the neglect of zero-point vibrational corrections can lead to a misinterpretation of the electron-density distribution in radicals for which the HFCCs of carbons are small. Therefore, zero-point vibrational corrections play a significant role in defining the magnitude and overall behavior of carbon isotropic HFCCs not only in semi-rigid molecules such as the methyl radical, but also in many ordinary organic π radicals, as has been demonstrated in this work.

In light of the results obtained in this work, we emphasize that the conventional methodology used for evaluating HFCCs, in which zero-point vibrational corrections are neglected, is not satisfactory for carbon HFCCs in organic π radicals and should be applied with care, especially for predicting carbon HFCCs with a small magnitude. Furthermore, we would advocate that the inclusion of zero-point vibrational corrections is essential when benchmarking different computational methods and when developing new exchange-correlation functional/basis sets combinations tailored for calculations of carbon HFCCs, because the neglect of these corrections can lead to an artificially better agreement between the theoretical and experimental data, as observed in our B3LYP calculations of carbon HFCCs in methyl and benzyl radicals, that would hide real physical contributions to the HFCCs. Similar conclusions have also been reached for other magnetic properties.[63]

[1]H. M. McConnell, J. Chem. Phys. **24**, 764 (1956).

[2]H. M. McConnell and D. B. Chesnut, J. Chem. Phys. **28**, 107 (1958).

[3]H. M. McConnell, Annu. Rev. Biophys. **39**, 1 (2010).

[4]F. Lendzian, M. Sahlin, F. MacMillan, R. Bittl, R. Fiege, S. Pötsch, B.-M. Sjöberg, A. Gräslund, W. Lubitz, and G. Lassmann, J. Am. Chem. Soc. **118**, 8111 (1996).

[5]G. Bleifuss, M. Kolberg, S. Pötsch, W. Hofbauer, R. Bittl, W. Lubitz, A. Gräslund, G. Lassmann, and F. Lendzian, Biochemistry **40**, 15362 (2001).

[6]H. S. Shafaat, B. S. Leigh, M. J. Tauber, and J. E. Kim, J. Am. Chem. Soc. **132**, 9030 (2010).

[7]I. Carmichael, J. Phys. Chem. **95**, 108 (1991).

[8]C. Adamo, V. Barone, and A. Fortunelli, J. Chem. Phys. **102**, 384 (1995).

[9]A. R. Al Derzi, S. Fau, and R. J. Bartlett, J. Phys. Chem. A **107**, 6656 (2003).

[10]R. Batra, B. Giese, M. Spichty, G. Gescheidt, and K. N. Houk, J. Phys. Chem. **100**, 18371 (1996).

[11]S. A. Perera, L. M. Salemi, and R. J. Bartlett, J. Chem. Phys. **106**, 4061 (1997).

[12]R. Improta and V. Barone, Chem. Rev. **104**, 1231 (2004).

[13]A. V. Arbuznikov, M. Kaupp, V. G. Malkin, R. Reviakine, and O. L. Malkina, Phys. Chem. Chem. Phys. **4**, 5467 (2002).

[14]V. Barone and A. Polimeno, Phys. Chem. Chem. Phys. **8**, 4609 (2006).

[15]L. Hermosilla, P. Calle, J. M. García de la Vega, and C. Sieiro, J. Phys. Chem. A **109**, 1114 (2005).

[16]S. Kossmann, B. Kirchner, and F. Neese, Mol. Phys. **105**, 2049 (2007).

[17]V. Barone, P. Cimino, and E. Stendardo, J. Chem. Theory Comput. **4**, 751 (2008).

[18]S. Kossmann and F. Neese, J. Phys. Chem. A **114**, 11768 (2010).

[19]S. Y. Chang, E. R. Davidson, and G. Vincow, J. Chem. Phys. **52**, 5596 (1970).

[20]Y. Ellinger, F. Pauzat, V. Barone, J. Douady, and R. Subra, J. Chem. Phys. **72**, 6390 (1980).

[21]V. Barone, A. Grand, C. Minichino, and R. Subra, J. Chem. Phys. **99**, 6787 (1993).

[22]K. Ohta, H. Nakatsuji, I. Maeda, and T. Yonezawa, Chem. Phys. **67**, 49 (1982).

[23]B. Fernandez, O. Christiansen, O. Bludsky, P. Jorgensen, and K. V. Mikkelsen, J. Chem. Phys. **104**, 629 (1996).

[24]H. Tachikawa, M. Igarashi, and T. Ishibashi, Chem. Phys. Lett. **352**, 113 (2002).

[25]K. Ruud, P. Åstrand, and P. R. Taylor, J. Chem. Phys. **112**, 2668 (2000).

[26]P.-O. Åstrand, K. Ruud, and D. Sundholm, Theor. Chem. Acc. **103**, 365 (2000).

[27]J. K. Kochi, P. Bakuzis, and P. J. Krusic, J. Am. Chem. Soc. **95**, 1516 (1973).

[28]S. Deycard, J. Lusztyk, K. U. Ingold, F. Zerbetto, M. Z. Zgierski, and W. Siebrand, J. Am. Chem. Soc. **110**, 6721 (1988).

[29]R. W. Fessenden and R. H. Schuler, J. Chem. Phys. **43**, 2704 (1965).

[30]X. Chen, Z. Rinkevicius, Z. Cao, K. Ruud, and H. Ågren, Phys. Chem. Chem. Phys. **13**, 696 (2011).

[31]P.-O. Åstrand, K. Ruud, and P. R. Taylor, J. Chem. Phys. **112**, 2655 (2000).

[32]K. Ruud, P. R. Taylor, and P.-O. Åstrand, Chem. Phys. Lett. **337**, 217 (2001).

[33]K. Ruud, P.-O. Åstrand, and P. R. Taylor, J. Am. Chem. Soc. **123**, 4826 (2001).

[34]J. Kongsted and K. Ruud, Chem. Phys. Lett. **451**, 226 (2008).

[35]Z. Rinkevicius, L. Telyatnyk, O. Vahtras, and H. Ågren, J. Chem. Phys. **121**, 7614 (2004).

[36]C. I. Oprea, L. Telyatnyk, Z. Rinkevicius, O. Vahtras, and H. Ågren, J. Chem. Phys. **124**, 174103 (2006).

[37]Z. Rinkevicius, K. J. de Almeida, and O. Vahtras, J. Chem. Phys. **129**, 064109 (2008).

[38]A. D. Becke, J. Chem. Phys. **98**, 5648 (1993).

[39]A. D. Becke, Phys. Rev. A **38**, 3098 (1988).

[40]C. Lee, W. Yang, and R. G. Parr, Phys. Rev. B **37**, 785 (1988).

[41]S. H. Vosko, L. Wilk, and M. Nusair, Can. J. Phys. **58**, 1200 (1980).

[42]A. Schafer, C. Huber, and R. Ahlrichs, J. Chem. Phys. **100**, 5829 (1994).

[43]T. A. Ruden, O. B. Lutnaes, T. Helgaker, and K. Ruud, J. Chem. Phys. **118**, 9572 (2003).

[44]S. Huzinaga, J. Chem. Phys. **42**, 1293 (1965).

[45]W. Kutzelnigg, U. Fleischer, and M. Schindler, *NMR Basic Principles and Progress* (Springer Verlag, Berlin, 1990), p. 165.

[46]Ch. vän Wullen, "Die Berechnung magnetischer Eigenschaften unter Berücksicht der Eletronkorrelation: Die Multikonfigurations-Verallgemeinerung der IGLO-Methode," Ph.D. dissertation, Ruhr-Universität, Bochum, 1992.

[47]S. A. Perera, J. D. Watts, and R. J. Bartlett, J. Chem. Phys. **100**, 1425 (1994).

[48]DALTON 2011, an *ab initio* electronic structure program, 2011, see http://www.daltonprogram.org.

[49]S. Y. Chang, E. R. Davidson, and G. Vincow, J. Chem. Phys. **52**, 1740 (1970).

[50]G. Vincow, S. Y. Chang, and E. R. Davidson, J. Chem. Phys. **54**, 4121 (1971).

[51]L. A. Eriksson, Mol. Phys. **91**, 827 (1997).

[52]C. Adamo, R. Subra, A. Di Matteo, and V. Barone, J. Chem. Phys. **109**, 10244 (1998).

[53]E. W. Stone and A. H. Maki, J. Am. Chem. Soc. **87**, 454 (1965).

[54]P. O'Malley and G. Babcock, J. Am. Chem. Soc. **106**, 817 (1984).

[55]W. M. Gulick and D. H. Geske, J. Am. Chem. Soc. **88**, 4119 (1966).

[56]M. R. Das and G. K. Fraenkel, J. Chem. Phys. **42**, 1350 (1965).

[57]P. J. O'Malley and G. T. Babcock, J. Am. Chem. Soc. **108**, 3995 (1986).

[58]L. A. Eriksson, F. Himo, P. E. M. Siegbahn, and G. T. Babcock, J. Phys. Chem. A **101**, 9496 (1997).

[59]P. J. O'Malley and S. J. Collins, Chem. Phys. Lett. **259**, 296 (1996).

[60]F. MacMillan, F. Lendzian, and W. Lubitz, Magn. Reson. Chem. **33**, S81 (1995).

[61]R. W. Fessenden, J. Phys. Chem. **71**, 74 (1967).

[62]A. M. Ihrig, P. R. Jones, I. N. Jung, R. V. Lloyd, J. L. Marshall, and D. E. Wood, J. Am. Chem. Soc. **97**, 4477 (1975).

[63]O. B. Lutnaes, A. M. Teale, T. Helgaker, D. J. Tozer, K. Ruud, and J. Gauss, J. Chem. Phys. **131**, 144104 (2009).

[64]D. Feller and E. R. Davidson, J. Chem. Phys. **88**, 7580 (1988).

[65]A. G. Davies, J. R. M. Giles, and J. Lusztyk, J. Chem. Soc., Perkin Trans. 2 **1981**, 747.

[66]P. Fuerderer and F. Gerson, J. Phys. Chem. **82**, 1125 (1978).