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Citation: J. Chem. Phys. **143**, 244306 (2015); doi: 10.1063/1.4938253
View online: https://doi.org/10.1063/1.4938253
View Table of Contents: http://aip.scitation.org/toc/jcp/143/24
Published by the American Institute of Physics

THE JOURNAL OF CHEMICAL PHYSICS **143**, 244306 (2015)

Ro-vibrational averaging of the isotropic hyperfine coupling constant for the methyl radical

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(Received 23 October 2015; accepted 8 December 2015; published online 24 December 2015)

We present the first variational calculation of the isotropic hyperfine coupling constant of the carbon-13 atom in the CH_3 radical for temperatures $T = 0$, 96, and 300 K. It is based on a newly calculated high level *ab initio* potential energy surface and hyperfine coupling constant surface of CH_3 in the ground electronic state. The ro-vibrational energy levels, expectation values for the coupling constant, and its temperature dependence were calculated variationally by using the methods implemented in the computer program TROVE. Vibrational energies and vibrational and temperature effects for coupling constant are found to be in very good agreement with the available experimental data. We found, in agreement with previous studies, that the vibrational effects constitute about 44% of the constant's equilibrium value, originating mainly from the large amplitude out-of-plane bending motion and that the temperature effects play a minor role. *© 2015 AIP Publishing LLC.* [http://dx.doi.org/10.1063/1.4938253]

I. INTRODUCTION

The importance of the nuclear motion contributions to various electromagnetic molecular properties is by now well understood.[1–19] The zero-point vibrational corrections (ZPVCs) are proved to be non-negligible for the electron paramagnetic resonance (EPR),[18,20] nuclear magnetic resonance (NMR),[8,15,21] and non-linear optical (NLO) properties.[9,22] The so-called pure vibrational contributions to NLO properties[23] are often comparable or even larger in magnitude than that due to electronic motions.[3,4,9–11] Moreover, some of the experimentally observed effects, such as temperature dependence and isotope shifts of electric and magnetic properties, are entirely due to the effect of molecular vibrations and rotations.[15]

Several successful methods for evaluating the ro-vibrational contributions to various molecular properties were formulated using the perturbation theory (PT) approach over the last few decades.[5,6,24,25] The applications of the PT-based approaches are however limited to quasi-rigid molecules vibrating harmonically within a single minimum potential energy surface (PES). For molecules exhibiting large amplitude anharmonic motions, due to the poor convergence of the PT expansion, the ro-vibrational wave functions and subsequent contributions to molecular properties must be obtained by variational methods. This, however, is much more computationally demanding and requires a more sophisticated numerical description of the PES. Thus, it is only applicable to small molecules. Only recently, a few general variational methods have been proposed capable of solving the ro-vibrational problem accurately for very highly excited states. These methods are routinely applicable to molecules with an arbitrary geometrical structure.[26–30] One of them, TROVE,[28,30] has been applied to compute the ZPVC-, temperature-, and isotope-dependence of the isotropic spin-spin coupling constants of NH_3.[15] The response theory approach has been developed for the vibrational configuration interaction method allowing accurate calculations of the pure vibrational contributions to the NLO properties.[31,32] In these and a few other[10,17,19] studies, the importance of a proper variational treatment of the large amplitude vibrations in obtaining accurate estimates of molecular properties has been emphasized.

In the present work, we report the first comprehensive variational calculations of the ro-vibrational contributions to the isotropic hyperfine coupling constant of the carbon-13 atom in the methyl radical CH_3, which we henceforth refer to as HFCC. The methyl radical is important in combustion processes and as an intermediate in many chemical reactions,[33] it has been observed in interstellar space,[34] and it is an example of a molecule with large vibrational contribution to HFCC that accounts for up to about 41% of the total value.[18] CH_3 has been the subject of many theoretical studies[35–46] characterizing the electronic structure and vibrational motion. The most recent works[45,46] reported the *ab initio* calculated PES and dipole moment surface and the variational ro-vibrational energy calculations for CH_3. Also, there have been a number of theoretical studies of the HFCC for $^{13}CH_3$.[18,47–49] To the best of our knowledge, in all previous studies of the HFCC, the vibrational effects were described by means of PT. In the present work, we have computed the new PES and HFCC surface for CH_3 in the ground electronic state. For the PES, we used the explicitly correlated coupled cluster CCSD(T)-F12 level[50] with the correlation consistent basis set cc-pVQZ-F12,[51] while the HFCC was computed

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by means of the conventional CCSD(T) with the augmented correlation consistent basis set aug-cc-pVTZ-J.[52,53] We expect these methods to yield an adequate accuracy for at least low energy levels, sufficient to converge the ro-vibrational contributions to HFCC at the room temperature and below. The PES and HFCC surface were used to compute the ro-vibrational energy levels, ZPVC, and temperature corrections to HFCC by means of the variational method TROVE.[28,30] The resulting vibrational energies and the total value of the HFCC at a temperature $T = 96$ K were found to be in good agreement with experiment, as well as with results of previous theoretical studies. For illustrative purposes, we compared the variationally computed expectation values of HFCC with those obtained from the perturbed-rigid-molecule (PRM) approach. As expected, the results confirm that PRM is not reliable for the expectation values of CH_3 in the excited out-of-plane bending states.

II. COMPUTATIONAL DETAILS

The calculations of the HFCC have been carried out within the framework of the Born-Oppenheimer approximation following a conventional three-step approach. First, the *ab intito* calculations of the ground state potential energy surface and the electronic contribution to HFCC are performed, which are followed by the calculations of the ro-vibrational energy levels and wave functions. The HFCC values associated with the ro-vibrational states of interest or their Boltzmann distribution are evaluated by averaging the *ab initio* HFCC function over the corresponding ro-vibrational wave functions.

(1) The electronic energies for the ground electronic state of CH_3 were computed on a grid of 22 640 symmetry-unique molecular geometries employing the open-shell RCCSD(T)-F12b[50,54] level of theory (explicitly correlated F12 restricted coupled cluster included single and double excitations with a noniterative correction for triples) and the F12-optimized correlation consistent polarized valence basis set cc-pVQZ-F12.[51] In correlated calculations, the carbon inner-shell electron pair was treated as a frozen core. The diagonal fixed-amplitude ansatz 3C(FIX)[55] and a Slater geminal exponent value of $\beta = 1.0$ (Ref. 56) were used. To evaluate the many-electron integrals in F12 theory, three additional auxiliary basis sets are required. For the resolution of the identity basis and the two density fitting basis sets, we utilized the corresponding OptRI,[57] cc-pV5Z/JKFIT,[58] and aug-cc-pwCV5Z/MP2FIT[59] basis sets, respectively. Calculations were carried out using the MOLPRO program.[60] The analytical representation for the PES was obtained in a least-squares fitting procedure using the functional form from Ref. 61. By varying 248 parameters, we achieved a fitting root-mean-square (rms) deviation of 0.9 cm^{-1}. The values of the fitted parameters are given in the supplementary material[62] together with a Fortran 90 routine for calculating the PES.

For the coupling-constant surface, the geometry-dependent values of the isotropic hyperfine coupling constant (also known as Fermi contact term) for carbon were obtained[63] as

$$A_{\text{iso}}^{(N)} = \frac{2}{3}\mu_0\,\mu_{\text{N}}\,g_{\text{N}}\,\rho(N) \tag{1}$$

for 19 959 symmetry-unique molecular geometries.

In Eq. (1), the index N labels a specific nucleus (carbon in our case), μ_0 is the vacuum permeability, μ_{N} is the nuclear magneton, g_{N} is the nuclear g factor, and $\rho(N)$ is the spin density at the carbon nucleus. The hyperfine coupling constant is an important parameter in EPR spectroscopy; it describes the hyperfine splitting and the positions of the resonance lines. A non-vanishing HFCC is due to interaction between the magnetic moments of the unpaired electron and the nuclei in the molecule. It is usually reported in the literature in units of magnetic field strength (G or T) and serves as a measure of the electronic magnetic spin interactions. To obtain the HFCC in Hz, the right hand side of Eq. (1) should be multiplied by the conversion factor $g_{\text{e}}\mu_{\text{B}}/h$ (Hz T^{-1}), where g_{e} is the g-factor of free electron, μ_{B} is the Bohr magneton, and h is the Planck constant. In the static view of CH_3 as a planar molecule, there is no direct contribution from the unpaired electron to the HFCC and the main contribution comes from spin polarization effects. The out-of-plane vibration allows and adds the direct contribution from the unpaired electron to the equilibrium value of the HFCC. We have calculated the HFCC employing the all-electron unrestricted open-shell CCSD(T) level of theory to account for spin polarization effects and the basis set aug-cc-pVTZ-J[52,53] designed to ensure the proper nuclear-cusp behaviour of the electronic wave function and thus a good description of the HFCC. The calculations were performed with the CFOUR program.[64] We have fitted the calculated points to the totally symmetric sixth-order power series expansion[65] in terms of six variables

$$\xi_k = (r_k - r_{\text{e}})\exp\left(-(r_k - r_{\text{e}})^2\right),\quad k = 1,2,3, \tag{2}$$

$$\xi_4 = (2\alpha_1 - \alpha_2 - \alpha_3)/\sqrt{6}, \tag{3}$$

$$\xi_5 = (\alpha_2 - \alpha_3)/\sqrt{2}, \tag{4}$$

$$\xi_6 = 1 - 2/\sqrt{3}\sin([\alpha_1 + \alpha_2 + \alpha_3]/6), \tag{5}$$

where $r_k - r_e$ denotes the displacement from the equilibrium value r_e of the distance between C and H_k, α_1, α_2, and α_3 are the instantaneous values of the bond angles $\angle(H_2\text{–}C\text{–}H_3)$, $\angle(H_1\text{–}C\text{–}H_3)$, and $\angle(H_1\text{–}C\text{–}H_2)$, respectively. The factor $\exp\left(-(r_k - r_{\text{e}})^2\right)$ in Eq. (2) ensures a physically reasonable asymptotic behaviour of the power series at large distances r_k.[66] In a least-squares fitting procedure, we determined 185 expansion parameters that reproduce the HFCC data with the rms of 0.11 G. The optimized parameters together with the Fortran 90 function for calculating the HFCC surface are given in the supplementary material.[62]

(2) The *ab initio* PES was used to compute the ro-vibrational energy levels of CH_3 employing the variational approach and computer program TROVE.[28,30] In TROVE, the ro-vibrational Hamiltonian is defined by the power-series expansions of its kinetic energy operator (KEO) and potential energy operator (PEO) in terms of internal coordinates around the equilibrium or reaction-path configuration. In the present work, the expansions of the kinetic and potential parts were truncated after the 6th and 8th order terms, respectively, and the six internal coordinates are three $r_i = \text{C–H}_i$ ($i = 1\ldots3$) stretching coordinates, two symmetry-adapted bending coordinates ξ_4 and ξ_5, as given in Eqs. (3) and (4),

and one out-of-plane bending coordinate τ (see Ref. 67 for details). The size of the vibrational basis set is controlled by the polyad number P,

$$P = 2(n_{r_1} + n_{r_2} + n_{r_3}) + n_{\xi_4} + n_{\xi_5} + n_{\tau}/2, \tag{6}$$

where n_i are the quantum numbers defined in connection with the primitive basis functions,[28] each describing ith vibrational degree of freedom. They are essentially the principal quantum numbers associated with the local mode vibrations of CH_3. The vibrational basis set contains only products of primitive functions for which $P \le P_{\max}$. We found that $P_{\max} = 10$ was sufficient to converge the vibrational energies below 7000 cm^{-1} to better than 0.05 cm^{-1} and the thermally averaged values of HFCC at a temperature $T = 300$ K to better than 0.002%. The ro-vibrational basis functions are generated as products of vibrational basis functions and symmetric-top rotational eigenfunctions and the ro-vibrational wave functions are obtained variationally by diagonalizing the full ro-vibrational Hamiltonian matrix.[28] Since TROVE uses symmetry-adapted basis functions and the total-angular-momentum quantum number J is a good quantum number, the diagonalization of the Hamiltonian matrix for each irreducible representation of the $\boldsymbol{D}_{3h}$ symmetry group, and each value of J, is done separately. Another important consequence of molecular symmetry is that the nuclear spin statistical factors[68] for the $\tilde{X}\ ^2A_2''$ electronic state of CH_3 are zero for the irreducible representations A_2' and A_2'', besides for each of the doubly degenerate representations E' and E'', only one degenerate component needs to be treated, thus reducing the total computational expenses for CH_3 by a factor of two. For CD_3, all statistical weight factors are non-zero; thus, only the second argument is viable.

(3) The vibrational and ro-vibrational expectation values of the HFCC were computed for $^{13}CH_3$ and $^{13}CD_3$ using the *ab initio* calculated coupling constant surface and the TROVE wave functions. The thermal average values for different temperatures were computed by summing over all ro-vibrational states the expectation values multiplied with the corresponding Boltzmann and degeneracy factors. For an ensemble of molecules in thermal equilibrium at absolute temperature T, the thermal average of the isotropic HFCC $A_{\rm iso}$ is given by

$$\langle A_{\rm iso}\rangle_T = \frac{1}{Q}\sum_i g_i \exp\left(-\frac{E_{\rm rv}^{(i)}}{kT}\right)\langle A_{\rm iso}\rangle_i, \tag{7}$$

where g_i is the degeneracy of the ith state with the energy $E_{\rm rv}^{(i)}$ relative to the ground state energy, k is the Boltzmann constant, Q is the internal partition function defined as

$$Q = \sum_i g_i \exp\left(-\frac{E_{\rm rv}^{(i)}}{kT}\right), \tag{8}$$

and $\langle A_{\rm iso}\rangle_i$ is the expectation value of the operator $A_{\rm iso}$ (which represents the HFCC) in the rovibrational state i,

$$\langle A_{\rm iso}\rangle_i = \langle \Phi_{\rm rv}^{(i)}|A_{\rm iso}|\Phi_{\rm rv}^{(i)}\rangle. \tag{9}$$

The calculation of the quantities in Eqs. (7)–(9) requires the eigenvalues $E_{\rm rv}^{(i)}$ and eigenvectors $\Phi_{\rm rv}^{(i)}$ which are obtained variationally with TROVE.

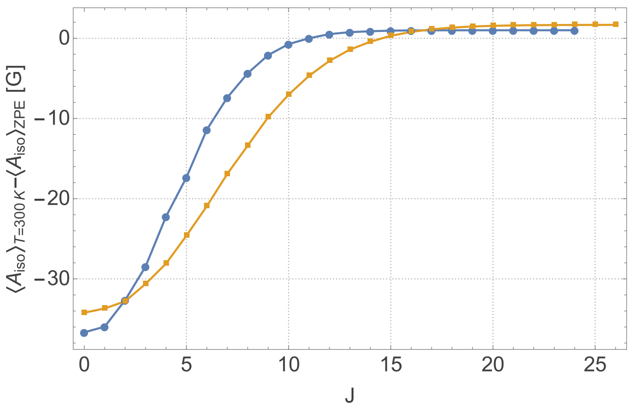

FIG. 1. Convergence of the $T = 300$ K thermally averaged HFCC vs $J_{\max}$ plotted for $^{13}CH_3$ (blue circles) and $^{13}CD_3$ (orange squares) relative to the ZPVC.

The degeneracy factor is computed as $(2J + 1)g_{\rm ns}$, where $g_{\rm ns}$ is the nuclear spin statistical weight taking values in D_{3h} symmetry group in the order (A_1', A_2', E', A_1'', A_2'', E'') as (8, 0, 4, 8, 0, 4) for $^{13}CH_3$ and (2, 20, 16, 2, 20, 16) for $^{13}CD_3$. (Note that the symmetry of the electronic wave function is A_2''.) The convergence of the thermal averaged values of HFCC at $T = 300$ K with respect to the maximal rotational excitation, defined by $J_{\max}$, is shown in Fig. 1. The values are plotted relative to the ZPVC (see Table IV). The energy spectrum of the heavier molecule CD_3 has a higher density than that of CH_3. In addition, CD_3 has more states allowed by spin statistics. Consequently, in CD_3, more ro-vibrational states become populated at a given temperature and so, higher J-values must be considered in the theoretical calculations in order to obtain converged values of the thermal averages. The computed values of the partition functions used to normalize the thermally averaged values for $T = 300$ K(96 K) are 737.08(127.10) for $^{13}CH_3$ and 7519.94(1194.11) for $^{13}CD_3$.

III. RESULTS

The planar equilibrium geometry of the electronic ground state, $\tilde{X}\ ^2A_2''$, of CH_3 has $\boldsymbol{D}_{3h}$ geometrical symmetry. The normal modes ν_1 and ν_2 of CH_3 have non-degenerate symmetries A_1' and A_2'', respectively, and associated principal quantum numbers v_1 and v_2. The normal modes ν_3 and ν_4 are of doubly degenerate symmetries E' and E'', respectively, the associated quantum numbers here are $v_3^{\ell_3}$ and $v_4^{\ell_4}$. The calculated 24 lowest vibrational energy levels of $^{12}CH_3$, $^{13}CH_3$, and $^{13}CD_3$ are listed in Table I where they are compared with the results of other theoretical studies[45,46] and experiment.[69–72] Each vibrational state is assigned by the symmetry in $\boldsymbol{D}_{3h}$(M) and vibrational quantum numbers $(v_1, v_2, v_3^{\ell_3}, v_4^{\ell_4})$ obtained from the basis function with the largest contribution to the vibrational eigenfunction. The agreement with experiment is generally good, the standard deviation for six states is 3.2 cm^{-1} which is a little improvement over the previous theoretical results of 4.6 cm^{-1} (Ref. 45) and 7.4 cm^{-1} (Ref. 46). The complete list of computed vibrational energies up to 8000 cm^{-1} for three isotopologues can be found in the supplementary material.[62]

TABLE I. Calculated and experimental vibrational energies (in cm^{-1}) for $^{12}CH_3$, $^{13}CH_3$, and $^{13}CD_3$.

		$^{12}CH_3$				$^{12}CH_3$	$^{12}CH_3$
$v_1\ v_2\ v_3^{\ell_3}\ v_4^{\ell_4}$	Γ[a]	Present work	Reference 45[b]	Reference 46[c]	Experiment[d]	Present work	Present work
$0\ 0\ 0^0\ 0^0$[e]	A_1'	[6466.9]	[6449.2]	[6445.9]	…	[6446.4]	[4742.1]
$0\ 1\ 0^0\ 0^0$	A_2''	601.1	596.3	591.7	606.5	596.1	447.4
$0\ 2\ 0^0\ 0^0$	A_1'	1278.3	1278.9	1266.2	1288.1	1267.7	944.6
$0\ 0\ 0^0\ 1^1$	E'	1389	1387.5	1388.4	1397	1384.1	1022.8
$0\ 1\ 0^0\ 1^1$	E''	2001.8	1997	1991.8	…	1992.1	1475.7
$0\ 3\ 0^0\ 0^0$	A_2''	2006	2025.6	1994.2	2019.2	1989.2	1476.4
$0\ 2\ 0^0\ 1^1$	E'	2688.8	2690	2674	…	2673.7	1977.6
$0\ 0\ 0^0\ 2^0$	A_1'	2752.4	2748.2	2750.7	…	2742.4	2022.6
$0\ 0\ 0^0\ 2^2$	E'	2770.9	2766.1	2767.8	…	2761.1	2039.5
$0\ 4\ 0^0\ 0^0$	A_1'	2771.8	2829	2763.2	…	2749.6	2034.9
$1\ 0\ 0^0\ 0^0$	A_1'	3003.4	2991.5	2988.5	3004.4	3002.6	2154.1
$0\ 0\ 1^1\ 0^0$	E'	3159.5	3144.6	3142.6	3160.8	3147.3	2362.0
$0\ 1\ 0^0\ 2^0$	A_2''	3378.6	3371.1	3367.1	…	3365.0	2482.5
$0\ 1\ 0^0\ 2^2$	E''	3395.2	3388.5	3382.9	…	3380.7	2498.3
$0\ 3\ 0^0\ 1^1$	E''	3426.6	3447	3407.5	…	3405.5	2514.0
$1\ 1\ 0^0\ 0^0$	A_2''	3595.1	3575.5	3572.8	…	3587.5	2595.2
$0\ 5\ 0^0\ 0^0$	A_2''	3564.5	3686	3557.7	…	3536.3	2616.8
$0\ 1\ 1^1\ 0^0$	E''	3736.2	3716	3710.2	…	3719.5	2793.7
$0\ 2\ 0^0\ 2^0$	A_1'	4075.1	…	4057.5	…	4056.1	2989.4
$0\ 2\ 0^0\ 2^2$	E'	4091.8	…	4073.1	…	4072.1	3005.2
$0\ 0\ 0^0\ 3^1$	E'	4128.4	…	4107.7	…	4114.7	3026.1
$0\ 0\ 0^0\ 3^3$	A_1'	4144.9	…	4138.9	…	4140.4	3053.9
$0\ 0\ 0^0\ 3^3$	A_2'	4150.1	…	4138	…	4135.4	3052.4
$0\ 4\ 0^0\ 1^1$	E'	4200.2	…	4179.7	…	4172.7	3076.2
$1\ 2\ 0^0\ 0^0$	A_1'	4258.4	…	4234.3	…	4246.0	3091.2

[a] Irreducible representation spanned by the wave function.

[b] ICMRCI+Q *ab initio* calculation.

[c] CASSCF-MR-CI *ab initio* calculation employing the aug-cc-pVTZ basis set.

[d] See Refs. 69–72.

[e] Zero-point energy.

The calculated expectation values of the HFCC for $^{13}CH_3$ given in Table II for a number of vibrational states show a very strong dependence on v_2, the quantum number of the out-of-plane vibration. This is due to both the nonrigid character of the out-of-plane motion and the strong dependence of the coupling constant on the out-of-plane coordinate (see Fig. 2). Even though we need to only consider one minimum of the PES here so that no tunneling motion takes place, the accurate treatment of the nonrigid character of the out-of-plane vibrational mode is very important. This is evident from the comparison (Table II) of HFCC expectation values obtained as described above with the results of a more conventional PRM approach, commonly used to compute vibrational corrections to molecular properties.[6,18] The PRM results in Table II were obtained variationally in the present work by expanding the TROVE Hamiltonian in normal coordinates with the KEO, PES, and HFCC parts truncated after zero-, quartic-, and second-order terms, respectively. All expectation values in Table II were obtained variationally but it is obvious that the use of normal coordinates and the restrictive truncation of the various series expansions introduce substantial changes in the expectation values. The PRM results deviate mostly from those of the nonrigid-model TROVE calculation for excited states of the out-of-plane bending mode. For such states, the deviations reach values around 10 G or 10%-20%. A "true" PRM calculation, using perturbation theory to solve the rovibrational Schrödinger equation, would introduce additional approximations and we surmise that it would produce results deviating even more from the nonrigid-model values. A complete list of HFCC vibrational expectation values for $^{13}CH_3$ and $^{13}CD_3$ is given in the supplementary material.[62]

In Table III, we give the theoretical equilibrium-geometry value of the HFCC for $^{13}CH_3$, the ZPVC, and the value resulting from the thermal averaging at $T = 96$ K. These values are compared with the results of the previous theoretical studies and experiment. In the previous theoretical studies, different electronic structure methods and basis sets were used to compute the potential and coupling constant surfaces and the vibrational corrections were treated by means of perturbation theory. As can be seen from the table, the HFCC value is strongly dependent on the ZPVC, which in this work is found to constitute about 44% of the equilibrium value. The temperature correction originating in excited rotation-vibration states (i.e., the correction obtained on top of ZPVC) at $T = 96$ K is 0.02 G and thus tiny; it obviously increases with increasing temperature and attains a value of 1.0 G (see Table IV) for $T = 300$ K. For $^{13}CD_3$, the ZPVC is approximately 25% of the equilibrium HFCC value (25.8 G); the additional $T = 300$ K temperature correction has a small value of 1.7 G.

TABLE II. Vibrational energies, E_{vib}, (in cm^{-1}) and expectation values of HFCC (in G) computed for $^{13}CH_3$ using the TROVE variational and the perturbed-rigid-molecule (PRM) approaches (see the text).

			HFCC	
$v_1\ v_2\ v_3^{l_3}\ v_4^{l_4}$	Γ[a]	E_{vib}	TROVE	PRM
$0\ 0\ 0^0\ 0^0$	A_1'	0.0	37.1	37.6
$0\ 1\ 0^0\ 0^0$	A_2''	596.2	52.8	55.8
$0\ 2\ 0^0\ 0^0$	A_1'	1267.7	64.5	70.5
$0\ 0\ 0^0\ 1^1$	E'	1384.1	39.4	38.6
$0\ 3\ 0^0\ 0^0$	A_2''	1989.2	74.6	83.1
$0\ 1\ 0^0\ 1^1$	E''	1992.2	54.6	57.0
$0\ 2\ 0^0\ 1^1$	E'	2673.7	66.0	71.6
$0\ 0\ 0^0\ 2^0$	A_1'	2742.4	52.2	40.2
$0\ 4\ 0^0\ 0^0$	A_1'	2749.6	76.0	93.9
$0\ 0\ 0^0\ 2^2$	E'	2761.1	42.9	39.6
$1\ 0\ 0^0\ 0^0$	A_1'	3002.6	39.0	39.3
$0\ 0\ 1^1\ 0^0$	E'	3147.3	38.5	39.6
$0\ 1\ 0^0\ 2^0$	A_2''	3364.9	58.7	58.2
$0\ 1\ 0^0\ 2^2$	E''	3380.7	57.6	67.7
$0\ 3\ 0^0\ 1^1$	E''	3405.5	75.5	73.9
$0\ 5\ 0^0\ 0^0$	A_2''	3536.3	90.5	101.5
$1\ 0\ 0^0\ 0^1$	A_2''	3587.5	55.9	58.2
$0\ 0\ 1^1\ 0^1$	E''	3719.5	54.6	58.5
$0\ 2\ 0^0\ 2^0$	A_1'	4056.1	68.9	72.3
$0\ 2\ 0^0\ 2^2$	E'	4072.1	67.7	72.3
$0\ 0\ 0^0\ 3^1$	E'	4114.7	51.7	41.6
$0\ 0\ 0^0\ 3^3$	A_2'	4135.4	44.7	40.6
$0\ 0\ 0^0\ 3^3$	A_1'	4140.9	49.9	40.6
$0\ 4\ 0^0\ 1^1$	E'	4172.7	84.5	93.1
$1\ 2\ 0^0\ 0^0$	A_1'	4246.0	67.2	86.2
$0\ 6\ 0^0\ 0^0$	A_1'	4353.7	98.5	94.9
$0\ 2\ 1^1\ 0^0$	E'	4371.5	66.3	72.4
$1\ 0\ 0^0\ 1^1$	E'	4385.0	42.3	40.3
$0\ 0\ 1^1\ 1^1$	A_2'	4510.3	40.6	40.5
$0\ 0\ 1^1\ 1^1$	E'	4518.1	40.9	40.3
$0\ 0\ 1^1\ 1^1$	A_1'	4526.4	41.6	40.6
$0\ 1\ 0^0\ 3^1$	E''	4742.2	63.5	58.9
$0\ 1\ 0^0\ 3^3$	A_2''	4765.3	62.9	67.9
$0\ 1\ 0^0\ 3^3$	A_1''	4766.1	58.7	59.0
$0\ 3\ 0^0\ 2^0$	A_2''	4801.4	78.1	74.0
$0\ 3\ 0^0\ 2^2$	E''	4813.1	77.8	83.1
$1\ 3\ 0^0\ 0^0$	A_2''	4959.3	76.8	80.6
$0\ 5\ 0^0\ 1^1$	E''	4964.7	83.7	99.9
$1\ 1\ 0^0\ 1^1$	E''	4984.3	66.4	59.5

[a] Irreducible representation spanned by the wave function.

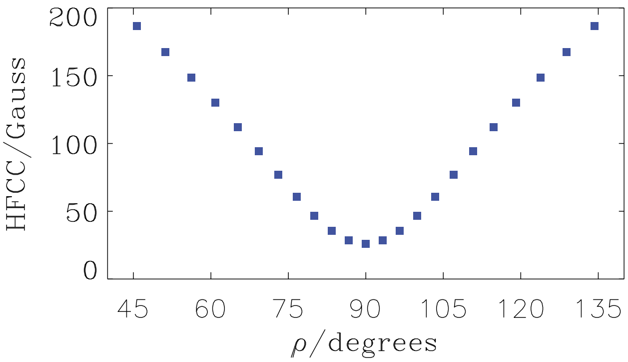

FIG. 2. The HFCC in $^{13}CH_3$ calculated at the CCSD(T)/aug-cc-pVTZ-J level of theory for molecular geometries with all three C–H bond lengths fixed at 1.0759 Å and all three H–C–H bond angles equal. The HFCC is plotted as a function of ρ, the angle between the three-fold rotational axis and any one of the three C–H bonds.

IV. DISCUSSION AND SUMMARY

Table III confirms that for the theoretical, thermally averaged values of the HFCC of $^{13}CH_3$, the differences between the value at equilibrium $A_{\mathrm{iso}}^{(\mathrm{eq})}$ and the vibrationally/thermally averaged value $A_{\mathrm{iso}}^{(\mathrm{tot})}$ are dramatic. As mentioned previously, these differences are solely due to the effect of the ZPVC. Analysis of the contributions from the individual vibrational modes has shown that the dominant vibrational effect originates from the out-of-plane bending mode (corresponding to the "umbrella-flipping" inversion of ammonia NH_3). Other vibrational modes contribute only slightly since the associated fundamental and overtone states are hardly populated at $T = 96$ K. In Fig. 2, we show the dependence of the HFCC in $^{13}CH_3$ on the out-of-plane vibrational coordinate ρ, which is defined as the angle between the three-fold rotational axis and any one of the three C–H bonds. Clearly, the strong dependence of the HFCC on ρ along with the effect of delocalization of the out-of-plane vibrational wave functions, due to the large amplitude character of the vibration, makes the corresponding expectation value and thus the contribution to the ZPVC quite substantial.

Our CCSD(T) equilibrium value $A_{\mathrm{iso}}^{(\mathrm{eq})}$ agrees well with the results of previous QCISD(T)[48] and MCSCF[49] (Multiconfigurational Self-Consistent-Field) calculations (Table III), with slightly larger deviation from the B3LYP result,[18] which is known to overestimate the spin polarization effect.[74] The

TABLE III. The calculated and experimental HFCC (in G) of $^{13}CH_3$. The values listed are the electronic HFCC at equilibrium geometry, $A_{\mathrm{iso}}^{(\mathrm{eq})}$, the total HFCC value including ZPVC ($T = 0$ K) and temperature ($T = 96$ K) correction, $A_{\mathrm{iso}}^{(\mathrm{tot})}$, as well values of the ZPVC (per temperature) effects with respect to the equilibrium.

Method/basis set	$A_{\mathrm{iso}}^{(\mathrm{eq})}$	$A_{\mathrm{iso}}^{(\mathrm{tot})}$	$A_{\mathrm{iso}}^{(\mathrm{tot})} - A_{\mathrm{iso}}^{(\mathrm{eq})}$	T (K)	Reference
P(CI)/DZ	22.2	35.1	12.9(58%)	96	47
QCISD(T)/TZVP	27.8	37.7	9.9(36%)	96	48
MCSCF/cc-pVTZus2st	27.7	37.3	9.6(35%)	0	49
B3LYP/Huz-IIIsu3	29.9	42.2	12.3(41%)	0	18
CCSD(T)/aug-cc-pVTZ-J	25.8	37.1	11.3(44%)	0/96	This work
Experiment	27.0	38.3	…	96	73

TABLE IV. Thermal contribution to HFCC (in G) in $^{13}CH_3$ and $^{13}CD_3$.

Temperature (K)	$^{13}CH_3$	$^{13}CD_3$
0	37.068	34.239
96	37.092	34.275
300	38.076	35.917

deviations can also be partly attributed to the effect of the different basis sets used in electronic structure calculations. We employed the basis set aug-cc-pVTZ-J, specifically designed for core properties. In several studies,[53,75,76] this basis set has proved to yield coupling constants in good agreement with experiment.

We conclude that with the high-level electronic structure method and comprehensive variational treatment of the ro-vibrational motion employed in the present work, we were able to obtain reliable values of the HFCC for $^{13}CH_3$ and $^{13}CD_3$ in very good agreement with experiment (Table III). In particular, we calculate realistically the large vibrational contribution to the HFCC, which we found to be 44% of the equilibrium value. In agreement with previous studies, the large vibrational contribution can be attributed to the large amplitude out-of-plane bending motion. For the temperatures considered in this study ($T < 300$ K), the thermal effects play a minor role.

ACKNOWLEDGMENTS

This work was supported in part by Grant No. JE 144/24-1 from the Deutsche Forschungsgemeinschaft (DFG), ERC Advanced Investigator Project No. 267219, and FP7-MC-IEF Project No. 629237. S.Y. acknowledges support from a "Tomsk State University Academic D.I. Mendeleev Fund Program" under Grant No. 8.1.51.2015.

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[63] In units of T (tesla), when all quantities on the right hand side of Eq. (1) are in SI units, another customary unit is the Gauss (G); 1 G = 10^{-4} T.

[64] CFOUR, a quantum chemical program package written by J. F. Stanton, J. Gauss, M. E. Harding, P. G. Szalay with contributions from A. A. Auer, R. J. Bartlett, U. Benedikt, C. Berger, D. E. Bernholdt, Y. J. Bomble, L. Cheng, O. Christiansen, M. Heckert, O. Heun, C. Huber, T.-C. Jagau, D. Jonsson, J. Jusélius, K. Klein, W. J. Lauderdale, F. Lipparini, D. A. Matthews, T. Metzroth, L. A. Mück, D. P. O'Neill, D. R. Price, E. Prochnow, C. Puzzarini, K. Ruud, F. Schiffmann, W. Schwalbach, C. Simmons, S. Stopkowicz, A. Tajti, J. Vázquez, F. Wang, J. D. Watts and the integral packages MOLECULE (J. Almlöf and P. R. Taylor), PROPS (P. R. Taylor), ABACUS (T. Helgaker, H. J. Aa. Jensen, P. Jørgensen, and J. Olsen), and ECP routines by A. V. Mitin and C. van Wüllen. For the current version, see http://www.cfour.de.

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